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VIOLACIÓN DE LA PARIDAD EN MOLÉCULAS QUIRALES

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Pedro Bargueño de Retes

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Isabel Gonzalo Fonrodona

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Índice general

1

Introducción

En esta tesis nos centramos en el estudio de los efectos de la interacción débil en moléculas quirales. Como es sabido, una molécula es quiral cuando ella misma y su imagen especular no se pueden superponer por medio de traslaciones o rotaciones. Las moléculas quirales presentan actividad óptica, es decir, diferente respuesta a la luz circularmente polarizada a derechas o a izquierdas, que en su aspecto dispersivo significa que el plano de luz linealmente polarizado que atraviese una muestra de moléculas de igual quiralidad sufre un giro a la derecha o a la izquierda dependiendo de si las moléculas son de una u otra quiralidad. Dicha quiralidad suele denotarse por L (de left o levógira) o R (right o dextrógira). Las dos conformaciones L y R, cada una imagen especular de la otra, son los dos enantiómeros de la molécula quiral.

Uno de los problemas más fascinantes, ligado a su vez al origen de la vida, es el origen de la homoquiralidad biológica, que consiste en que las moléculas quirales de los seres vivos sólo presentan una de las dos quiralidades, estando completamente ausente la otra. Por ejemplo, todos los aminoácidos son levógiros y los azúcares dextrógiros. Se han propuesto varios mecanismos de discriminación quiral que puedan explicar dicha asimetría pero, hasta el momento, ninguno resulta suficientemente convincente. Uno de ellos es la violación de la paridad en la interacción débil, presente en átomos y moléculas. En átomos, dicha interacción se ha detectado experimentalmente mientras que en moléculas no se ha podido detectar hasta la fecha. En particular, la interacción débil predice una pequeña diferencia energética entre los dos enantiómeros de una molécula quiral (del orden de 10^{-16} eV) que, junto con procesos de amplificación apropiados, podría producir una discriminación quiral a favor de una única de las conformaciones, L o R.

En esta tesis nos hemos centrado en el efecto de la interacción débil en moléculas quirales, no ya sólo porque pudiera ser el origen de la homoquiralidad biológica, sino por la variedad de fenómenos que puede provocar en dichas moléculas, algunos de los cuales podrían emplearse para detectar experimentalmente la diferencia energética predicha entre los dos enantiómeros.

Primeramente hemos abordado el efecto discriminatorio sobre conformaciones L y R que puede aparecer por la interacción débil entre neutrinos y moléculas quirales. A continuación nos hemos centrado en los efectos que tendría la diferencia energética predicha entre los dos enantiómeros en la dinámica interna que presentan dichas moléculas suficientemente aisladas. Dicha dinámica consiste en la interconversión de las conformaciones L y R por efecto túnel a través de una barrera de potencial de un doble pozo de potencial donde cada mínimo corresponde a una de las dos conformaciones. En este sentido, hemos estudiado la modificación que sufre la actividad óptica oscilante, así como los efectos termodinámicos asociados a la violación de la paridad, tanto para un gas de Maxwell–Boltzman como para uno de Bose–Einstein de moléculas quirales, sugiriendo varios experimentos para detectar la mencionada diferencia de energía electrodébil entre enantiómeros, uno de ellos asociado al fenómeno de resonancia estocástica.

A continuación, hemos restringido el valor de una constante de acoplo que implica violación de la paridad en la interacción gravitatoria, teniendo en cuenta que dicha interacción da lugar a una diferencia de energías entre enantiómeros opuestos (todavía no detectada).

Finalmente, hemos tratado efectos disipativos al considerar la interacción ente moléculas quirales, donde la contribución de la violación de la paridad no parece ser tan importante comparada con otras interacciones moleculares. Sin embargo, dicha disipación tiene interés a efectos del atrapamiento que puede producirse en una única de las conformaciones quirales.

En lo que sigue se hará primero un repaso de los antecedentes que hay en la lieratura científica sobre el tema de la tesis, para continuar con una somera exposición de los trabajos realizados que constituyen el cuerpo principal de la misma. A lo largo de dicha exposición se irá haciendo referencia a los artículos publicados a los que ha dado lugar este trabajo, los cuales se incluyen íntegramente al final de esta exposición. Por último, se resumen las conclusiones en un apartado final.

2

Hipótesis sobre el origen de la homoquiralidad

A lo largo de los años se han propuesto diferentes hipótesis a partir de las cuales se pretende dilucidar cuál es el origen de la homoquiralidad biomolecular [1–3]. Debido a la absoluta falta de consenso existente entre los miembros de la comunidad científica sobre su plausibilidad, resulta útil caracterizarlas. Una posible clasificación se basa en la respuesta a si existe algún mecanismo de carácter quiral causante del origen de la homoquiralidad molecular. Si la respuesta es afirmativa, entonces diremos que la teoría que la sustenta es *determinista*. En caso contrario, diremos que dicha teoría está basada en el puro *azar* (en el sentido de aleatoriedad).

2.0.1. Teorías basadas en el azar

En principio, estas teorías no son comunmente aceptadas porque estamos acostumbrados a poder reproducir los experimentos. Lo opuesto sería la manifestación macroscópica de un único evento estocástico, que daría lugar, cada vez que se repitiese el experimento, a un resultado completamente aleatorio (además, si los procesos aleatorios dieran como resultado un pequeño exceso de una quiralidad determinada, en otra región (del espacio o del tiempo) dicho exceso podría ser de la otra quiralidad). En general, las reacciones químicas que responden a este patrón son meras entidades teóricas, con excepción de la reacción de Soai, recientemente descubierta. Dicha reacción se basa en procesos autocatalíticos, en los que los productos de reacción son a su vez catalizadores de la misma.

Modelo de Frank

Un ejemplo sencillo de la aplicación de la autocatálisis en la quiralidad molecular viene descrito por el modelo de Frank [4]: supongamos un reactor que se alimenta con moléculas aquirales, A y B, que reaccionan para dar lugar a los productos quirales L y R. Como el proceso es autocatalítico, los productos quirales, L y R, catalizan su propia formación según las ecuaciones:

$$\begin{aligned} A+B &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} L \\ A+B &\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R \\ A+B+L &\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2L \\ A+B+R &\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2R \\ L+R &\xrightarrow{k_3} P, \end{aligned} \tag{2.1}$$

donde P representa un producto inactivo que se expulsa del reactor para permitir que el sistema sea estacionario. Es importante notar que, si consideramos L y R moléculas isoenergéticas, se tiene que $k_1 = k_2$ y $k_{-1} = k_{-2}$.

Las ecuaciones cinéticas del modelo de Frank son

$$\begin{aligned} \frac{d[L]}{dt} &= k_1[A][B] - k_{-1}[L] + k_2[A][B][L] - k_{-2}[L]^2 - k_3[L][R] \\ \frac{d[R]}{dt} &= k_1[A][B] - k_{-1}[R] + k_2[A][B][D] - k_{-2}[D]^2 - k_3[L][R]. \end{aligned} \tag{2.2}$$

Si introducimos el cambio de variables $\lambda = [A][B]$, $\alpha = \frac{[L]-[R]}{2}$ y $\beta = \frac{[L]+[R]}{2}$, es sencillo derivar la ecuación

$$\frac{d\alpha}{dt} = -A\alpha^3 + B(\lambda - \lambda_c\alpha), \tag{2.3}$$

donde A y B toman valores constantes que dependen de las constantes de reacción.

Para $\lambda > \lambda_c$, donde λ_c es cierto valos crítico, el sistema se vuelve metaestable, dando lugar espontáneamente a estructuras homoquirales pero equiprobables. Por el contrario, cuando $\lambda < \lambda_c$, el sistema es racémico ($[L] = [R]$). Tal y como se comentó previamente, un ejemplo de reacción autocatalítica que produce asimetría quiral de manera simple y que, además, ha sido experimentalmente observada, es la reacción de Soai [5].

Nótese que la equiprobabilidad de las citadas estructuras homoquirales no se mantiene al introducir una perturbación quiral, por ejemplo, debido a efectos moleculares electrodébiles, tal y como contempla, por ejemplo, el modelo de Kondepudi [6].

2.0.2. Teorías deterministas

Podemos clasificar a su vez las teorás deterministas en *locales* y *universales*. Teorías locales son aquellas en las que la influencia quiral inicial existió únicamente en cierta región del espacio (o del tiempo). En caso contrario, diremos que una teoría determinista es universal cuando dicha influencia quiral es permanente y omnipresente.

Mecanismos locales

β–radiólisis

Las desintegraciones β están gobernadas por la interacción débil y, por lo tanto, los electrones emitidos en dichos procesos son inherentemente quirales en el sistema de laboratorio (esto es, son una influencia realmente quiral, según la nomenclatura adoptada por Barron [7, 8]). Específicamente, dicha quiralidad crece con la velocidad a la que circulan. A medida que la radiación β atraviesa la materia, se frena mediante radiación *Bremsstrahlung*, la cual está circularmente polarizada (en el mismo sentido en que lo está la radiación β original). La base teórica para dicho mecanismo, propuesto originalmente por Vester y Ulbricht [9] inmediatamente después del descubrimiento de la violación de la paridad en la interacción débil, fue desarrollada por Hegstrom a comienzos de los años 80 [10] (por lo tanto, no es casual que el propio

Hegstrom fuera uno de los pioneros en realizar cálculos electrodébiles en moléculas quirales [11]). A pesar de la plausibilidad de dicha hipótesis, todos los esfuerzos por confirmarla en el laboratorio han resultado infructuosos [12]. Además, existe otro mecanismo anterior a la β–radiólisis que pudo haber provocado la homoquiralidad biológica ya que se han encontrado meteoritos con una exceso considerable de L–aminocidos [13–15]. Por lo tanto, situando el origen de la homoquiralidad fuera de la Tierra, todos los mecanismos terrestres, en particular la β–radiólisis, quedan descartados.

Luz circularmente polarizada

Según la definición dada por Barron, la luz circularmente polarizada (LCP) es otro ejemplo de influencia realmente quiral [8]. Por lo tanto, en principio debería ser capaz de producir procesos fotoquímicos asimétricos. Dada la quiralidad intrńseca de la luz CP, su interacción con una molécula quiral no es igual en caso de tratarse de R–LCP o de L–LCP, resultando en una absorción diferente de L–LCP y R–LCP (dicroísmo circular). Dicha interacción puede dar lugar tanto a fotodegradación asimétrica como a fotosíntesis asimétrica [16].

- LCP en la Tierra

  La luz natural, así como las fuentes usuales de luz incandescente, icluyendo las llamas y la luz del Sol, no está polarizada. Aun así, bajo ciertas condiciones, en la Tierra se producen de manera natural pequeñas cantidades de LCP [17]. El problema es que la rotación de la Tierra hace que el promedio de LCP a lo largo de un ciclo diurno se anule. Por lo tanto, es necesario invocar la existencia de mecanismos alternativos (por el momento desconocidos) que introduzcan algún tipo de asimetría quiral.

  Otra posible fuente de LCP se debe al efecto Faraday, que resulta de la interacción entre la luz solar y el campo magnético terrestre. Aunque este efecto tiene signo opuesto en cada hemisferio y su promedio no se cancela debido al carácter elíptico de la órbita terrestre alrededor del Sol, el efecto que puede producir como origen de la discriminación quiral es pequeño [18].

- LCP en el espacio exterior

Como ya se comentó anteriormente, se han encontrado meteoritos con un exceso enentiomérico considerable. Por lo tanto, los mecanismos quiroselectores que operan en el espacio exterior son de especial interés. En este sentido, es importante señalar las hipótesis de Rubenstein y Bonner [19, 20] sobre el posible origen de la homoquiralidad en la radiación emitida por las estrellas de neutrones. De hecho, se ha encontrado LCP proveniente de dichas estrellas. Ahora bien, los aminoácidos tienen bandas de absorción en el ultravioleta (200-250 nm) y únicamente se ha encontrado LCP en el infrarrojo y en radiofrecuencias [21]. Finalmente, Bailey propuso que las LCP emitida en las regiones de formación estelar podría contribuir a crear el exceso enantiomérico observado [22], aunque este mecanismo todavía no ha podido ser confirmado.

- Dicroísmo magneto–quiral

  En 1982, Wagniere y Meier predijeron que un campo magnético estático paralelo a la dirección de propagación de un haz de luz incidente (incluso sin ser LCP) causa un pequeño desplazamiento en el valor del coeficiente de absorción de una molécula quiral (de signo distinto para enantiómeros opuestos) [23]. Utilizando este efecto, observado en 1997 por Rikken y Raupach [24], ha sido posible producir un único enantiómero en una reacción fotoquímica [25]. Por lo tanto, el dicroísmo magneto–quiral juega actualmente un papel muy importante en las teorías que consideran que el origen de la homoquiralidad es consecuencia de campos magnéticos cósmicos [26], principalmente debido a que, como ya hemos comentado, el citado mecanismo no necesita de LCP (no muy frecuente en el espacio exterior) para funcionar.

Mecanismos universales

Interacción electrodébil núcleo–electrón en moléculas quirales

El mecanismo quiroselector universal por excelencia se debe a la interacción débil. De las cuatro fuerzas que operan en el Universo (electromagnética, gravitatoria, nuclear fuerte y nuclear débil), solo ésta última es capaz de diferenciar *izquierda* de *derecha*. Formalmente, esto puede expresarse como

$$[H^{PV}, P] \neq 0, \tag{2.4}$$

donde H^{PV} representa el Hamiltoniano de la interacción débil y P es el operador de paridad. Como se mostrará en el siguiente capítulo, en el que se describirá con más detalle la interacción electrodébil electrón–núcleo, la unificación electrodébil predice una diferencia de energía entre dos enantiómeros moleculares, descritos mediante los estados L y R, tal que [27]

$$\langle L|H^{EW}|L\rangle = -\langle R|H^{EW}|R\rangle = \epsilon_{PV}, \tag{2.5}$$

por lo tanto, se define la PVED (del inglés, *parity violating energy difference*) como

$$\Delta E_{PV} \equiv \langle L|H^{EW}|L\rangle - \langle R|H^{EW}|R\rangle = 2\epsilon_{PV}, \tag{2.6}$$

donde H^{EW} es el Hamiltoniano electrodébil que describe la interacción electrón–núcleo. Considerando la aproximación no relativista para los nucleones y sin tener en cuenta el espín nuclear, el Hamiltoniano electrodébil efectivo que describe la interacción entre n electrones y N núcleos moleculares resulta ($c = \hbar = 1$) [28]

$$H^{EW} = \frac{G_F}{2\sqrt{2}m} \sum_{i=1}^{n} \sum_{A=1}^{N} Q_W(A)\{\mathbf{p}_i \cdot \mathbf{s}_i, \rho\,(\mathbf{r}_i - \mathbf{r}_A)\}, \tag{2.7}$$

donde G_F es la constante de Fermi ($G_F = 1{,}16637(1)\,10^{-5}$ GeV^{-2}), $\mathbf{p}_i$ y $\mathbf{s}_i$ son, respectivamente, el momento y el espín del i–ésimo electrón y $\rho\,(\mathbf{r}_i - \mathbf{r}_A)$ es la densidad nuclear expresada en función de la distancia electrón–núcleo. La carga débil de un núcleo con Z protones y $N = Z - A$ neutrones se puede expresar como $Q_W(A) = (1 - 4\sin^2\theta_W)Z - N$, donde θ_W es el ángulo de Weinberg, cuyo valor aproximado viene dado por $\sin^2\theta_W \approx 0{,}23$ [30].

Así, aunque se prevée que esta pequeña diferencia de energías (nótese que la escala de energías electrodébil es del orden de 10^{-16} eV) tiene consecuencias a nivel molecular, todavía no se tiene constancia experimental de su existencia [31, 32] contrariamente a lo que ocurre en los átomos, en los que si se ha detectado [33].

Una forma sencilla de ver la relación causa–efecto entre violación de la paridad y homoquiralidad molecular es mediante el modelo de Kondepudi [6]. La amplitud de la disimetría quiral, α, viene regida por la ecuación de Langevin

$$\frac{d\alpha}{dt} = -A\alpha^3 + B(\lambda - \lambda_c\alpha) + Cg + C'\eta f(t), \tag{2.8}$$

donde $g \equiv \Delta E/kT$ es el factor que hace que las constantes de reacción para los enantiómeros L y R difieran debido a la violación de la paridad, $k_L = k_R(1+g)$. Además de dichos efectos, el término $C'\eta f_2(t)$ representa fluctuaciones aleatorias. Considerando $g \neq 0$, el sistema se vuelve metaestable para $\lambda > \lambda_c$, dando lugar espontáneamente a estructuras homoquirales pero no equiprobables. Esto es, la pequeña contribución de g hace que se seleccione, de manera espontánea, uno de los dos enantiómeros. En concreto, Kondepudi estimó que, considerando $g \approx 10^{-17}$ (lo cual es muy razonable teniendo en cuenta el orden de magnitud de la PVED), una muestra racémica de moléculas inmersas en un recipiente de 1 km^2 superficie y 1 m de profundidad (digamos, un lago) necesitaría un tiempo de 10^4 años para evolucionar de manera espontánea hacia un estado quiral con una probabilidad de aproximadamente 98 %. De esta manera, conceptualmente sencilla, puede derivarse la homoquiralidad molecular a partir de la violación de la paridad en la interacción electrodébil.

Interacción electrodébil neutrino (WIMP)–electrón en moléculas quirales

Otro mecanismo universal, aportación de esta tesis (del que hablaremos en la próxima sección), que podría discriminar entre los dos enantiómeros de una molécula quiral, y que además involucra la interacción débil, es la interacción entre los neutrinos (tanto los provenientes de una explosión de supernova como los de origen cosmolgico) y los electrones de una molécula quiral [34–37]. Teniendo en cuenta que los electrones de enantiómeros opuestos tienen opuesta helicidad, este proceso es discriminatorio en tanto en cuanto exista una asimetría en el número de neutrinos y de antineutrinos. Específicamente, la diferencia de energías entre enantiómeros monoelectrónicos puede obtenerse a partir de un Hamiltoniano similar al de la Ec. (2.7) considerando la aproximación no relativista para los neutrinos, obteniendo [35]

$$\Delta E_\nu \sim G_F(n_\nu - n_{\bar{\nu}}) \sum_i \langle L|\mathbf{p}_i \cdot \mathbf{s}_i|L\rangle, \tag{2.9}$$

donde $n_\nu - n_{\bar{\nu}}$ es la diferencia en la densidad de número de neutrinos y antineutrinos y $\langle L|\mathbf{p}_i \cdot \mathbf{s}_i|L\rangle$ es, básicamente, la helicidad electrónica de uno de los dos enantiómeros (en caso de tratarse de neutrinos provenientes de una explosión de supernova, nos encontramos frente a un mecanismo discriminatorio de quiralidad *universal pero local* [36]).

De manera análoga al caso anterior, la materia oscura también ha sido propuesta como posible mecanismo inductor de homoquiralidad [38]: la diferencia de energías entre dos enantiómeros debido a la interacción entre WIMPs fermiónicos (del inglés, *weakly interacting massive particles*), que son candidatos no bariónicos a materia oscura fría, y electrones moleculares puede escribirse como

$$\Delta E_\chi \sim d_e \alpha \frac{\rho}{M_\chi} \sum_i \langle L|\mathbf{p}_i \cdot \mathbf{s}_i|L\rangle, \tag{2.10}$$

donde M_χ y ρ son, respectivamente, la masa y densidad (de energía) de los WIMPs, α señala la diferencia entre el número de WIMPs y el de anti–WIMPs y d_e es la constante acoplamiento WIMP–electrón.

Es importante notar que estos mecanismos discriminatorios dependen de manera crucial de:

- la asimetría neutrino–antineutrino en el baño cosmológico (no detectado, se conocen algunas cotas) [39]
- la masa del WIMP y su constante de acoplo con el electrón (desconocidas, se conocen algunas cotas) (una información actualizada se puede encontrar en [40])

Por lo tanto, las consecuencias que los mismos puedieran tener sobre la homoquiralidad molecular hay que tomarlas con cautela.

3

Efectos electrodébiles en moléculas quirales

En esta sección primero describimos los métodos para pasar a continuación a describir someramente los trabajos que constituyen el cuerpo de esta tesis. Nuestro principal interés es mostrar cómo es posible introducir efectos electrodébiles en la descripción de moléculas quirales. Para ello, necesitamos una descripción rigurosa de la interacción entre los núcleos y los electrones de dichas moléculas, incluyendo el intercambio de bosones Z^0.

3.0.3. Hamiltoniano pseudoescalar y principales características

De acuerdo al Modelo Estándar [41–43], los mediadores de la interacción que nos interesa son los bosones gauge neutros, Z^0. A energías menores que la masa en reposo de dicho bosón, esto es, menores que 91.19 GeV, su contribución se vuelve virtual y puede escribirse como un producto entre una *corriente vectorial* y una *corriente axial* [44]. Por lo tanto, lo que primero tenemos que describir son las corrientes vectoriales

$$j^\mu \equiv: \psi^\dagger(x)\gamma^0\gamma^\mu\psi(x) : \tag{3.1}$$

y las axiales

$$j^{\mu}_{ax} \equiv : \psi^{\dagger}(x)\gamma^0\gamma^{\mu}\gamma^5\psi(x) :, \tag{3.2}$$

donde los dos puntos representan el ordenamiento normal de los operadores (esto es, todos los operadores de destrucción aparecen a la derecha de los de creación), γ^0, γ^{μ} y γ^5 son las matrices de Dirac [30] y ψ es un biespinor de cuatro componentes ($\psi^{\dagger}$ es su traspuesto conjugado). Recalquemos que la presencia de la matrix γ^5 es muy importante ya que es muy útil para introducir el concepto de quiralidad desde el punto de vista mecanocuántico [45].

A bajas energías, la interacción débil entre dos fermiones se puede escribir a partir de la siguiente densidad Hamiltoniana efectiva [28, 29, 33]

$$H^{eff}(x) = -\frac{G_F}{\sqrt{2}} : \bar{\psi}_1(x)\gamma^{\mu}(g_V^{\psi_1} - g_A^{\psi_1}\gamma^5)\psi_1(x)\bar{\psi}_2(x)\gamma_{\mu}(g_V^{\psi_2} - g_A^{\psi_2}\gamma_5)\psi_2(x) :, \tag{3.3}$$

donde $\bar{\psi}_i \equiv \psi_i^{\dagger}\gamma^0$ denota el espinor adjunto a ψ_i, el cual describe al i–ésimo fermión y $g_{V,A}^{\Psi_i}$ son constates de acoplamiento (vectoriales o axiales) correspondientes a dicho fermión.

Como queremos describir la interacción débil entre los electrones de una molécula quiral con todos los nucleones que constituyen el núcleo de la misma, podemos generalizar de manera inmediata la Ec. (3.3) quedando

$$H^{eff}(x) = -\frac{G_F}{\sqrt{2}} \sum_i : \bar{\psi}_i(x)\gamma^{\mu}(g_V^{\psi_i} - g_A^{\psi_i}\gamma^5)\psi_i(x)\bar{e}(x)\gamma_{\mu}(g_V^{e} - g_A^{e}\gamma_5)e(x) :, \tag{3.4}$$

donde $e(x)$ corresponde al biespinor del electrón y la suma se efectúa para todos los nucleones $\psi_i(x)$.

Si asumimos que el movimiento de los nucleones es no–relativista, podemos escribir la parte espacial del cuardriespinor de Dirac de un nucleón infinitamente masivo como

$$u_j(\mathbf{r}) \approx \begin{pmatrix} \chi(\mathbf{r}) \\ \frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2m_j i}\chi(\mathbf{r}) \end{pmatrix} \approx \begin{pmatrix} \chi(\mathbf{r}) \\ 0 \end{pmatrix}. \tag{3.5}$$

En este límite se obtiene

$$
\begin{aligned}
\bar{u}_j(\mathbf{r})\gamma^0 u_j(\mathbf{r}) &\approx \chi_j^+(\mathbf{r})\chi_j(\mathbf{r}) = \rho_j(\mathbf{r}) \\
\bar{u}_j(\mathbf{r})\boldsymbol{\gamma} u_j(\mathbf{r}) &\approx \mathbf{0} \\
\bar{u}_j(\mathbf{r})\gamma^0\gamma^5 u_j(\mathbf{r}) &\approx 0
\end{aligned}
\tag{3.6}
$$

donde $\rho_j(\mathbf{r})$ es la distribución de densidad del j–ésimo nucleón. Tomando idénticas distribuciones de protones y de neutrones se tiene que la densidad promedio es [28, 29]

$$
\langle\rho(\mathbf{r})\rangle \approx (Zg_V^p + Ng_V^n) = \frac{1}{2}[(1-4\sin^2\theta_W)Z - N]\rho(\mathbf{r}) = \frac{1}{2}Q_W\rho(\mathbf{r}), \tag{3.7}
$$

donde Q_W es la *carga débil* del núcleo y θ_W es el ángulo de Weinberg (ver apartado anterior). La relación entre las constantes de acoplamiento y dicho ángulo se puede escribir como [29]

$$
\begin{aligned}
g_A^p &= \frac{1}{2}(1-4\sin^2\theta_W) \approx 0{,}04 \\
g_A^n &= -\frac{1}{2} \\
g_V^p &= \frac{1}{2}(1-4\sin^2\theta_W)\,1{,}26 \approx 0{,}05 = -g_V^n.
\end{aligned}
\tag{3.8}
$$

Nótese que, como $\sin^2\theta_W \approx 0{,}23$, la carga débil es proporcional al número de neutrones, $Q_W(A) \approx N$.

Respecto a la parte electrónica, teniendo en cuenta que, en el límite no relativista,

$$
e(\mathbf{r}) = \begin{pmatrix} \sqrt{\frac{E+m}{2m}}\chi(\mathbf{r}) \\ \frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2m}\chi(\mathbf{r}) \end{pmatrix}, \tag{3.9}
$$

se tiene que [46]

$$
\bar{e}(\mathbf{r})\gamma^0\gamma^5 e(\mathbf{r}) \approx -\left(\chi^+(\mathbf{r})\frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2m}\chi(\mathbf{r})\right) + \left(\chi(\mathbf{r})\frac{\boldsymbol{\sigma}\cdot\mathbf{p}}{2m}\right)^+\chi(\mathbf{r}). \tag{3.10}
$$

Finalmente, reordenando todos los términos se llega a que la parte que viola la paridad de la interacción entre los n electrones y los N núcleos que conforman la molécula es

$$H^{EW} = \frac{G_F}{2\sqrt{2}m} \sum_{i=1}^{n} \sum_{A=1}^{N} Q_W(A) \{\mathbf{p}_i \cdot \mathbf{s}_i, \rho(\mathbf{r}_i - \mathbf{r}_A)\}, \tag{3.11}$$

que es la expresión (2.7) a la que se hizo mención anteriormente.

Nótese que, a lo largo de la derivación de la Ec. (3.11), se han despreciado términos dependientes del espín nuclear. Al contrario que los términos independientes del espín nuclear, los nucleones no contribuyen coherentemente (nótese que la carga débil crece con Z). En el modelo de capas, únicamente el nucleón desapareado contribuye al espín nuclear total. Además, el valor del término $(1 - \sin^2 \theta_W)$ que acompaña a dichos términos es pequeño en el Modelo Estándar. Por lo tanto, al menos cuando tratemos con moléculas que contengan átomos pesados, es lícito despreciar los términos dependientes del espín nuclear frente a los independientes del mismo.

Para finalizar este apartado resaltemos que, como consecuencia del carácter pseudoescalar de H^{EW} que aparece debido al término de helicidad electrónica de la Ec. (3.11), la degeneración energética existente entre dos enantiómeros opuestos (consecuencia de la conservación de la paridad en la interacción electromagnética), se rompe. Por lo tanto, queda demostrado que

$$\Delta E_{PV} \equiv \langle L|H^{EW}|L\rangle - \langle R|H^{EW}|R\rangle = 2\epsilon_{PV} \equiv 2\epsilon \neq 0. \tag{3.12}$$

3.0.4. Modelo Harris-Stodolsky

Una posible descripción mecanocuántica de los efectos de violación de la paridad en moléculas quirales puede lograrse ampliando el modelo de Hund del doble pozo simétrico [47] al caso asimétrico. Tal y como notaron Lethokov y otros [48–50], el hecho de que los dos enantiómeros tuvieran diferentes energías como consecuencia de la violación de la paridad, podía representarse como una asimetría entre ambos pozos, tal y como muestra la Fig. (3.1). En relación a la *paradoja de Hund* (por qué ciertas moleculas aparecen en estados quirales si éstos no son autoestados del Hamiltoniano), Harris y Stodolsky mostraron cómo este sencillo modelo predice la localización de los estados quirales (en ausencia de interacciones), para aquellas moléculas en las que la violación de la paridad resulta dominante frente a la transformación de un enantiómero en otro por efecto túnel [51]. Los efectos de la violación de la paridad, haciendo uso de este sencillo modelo, también han sido frecuentemente considerados por Quack [52, 53]. Aunque el uso del modelo de dos estados para describir moléculas quirales es comunmente aceptado, sobre todo en cuanto al estudio de sus propiedades dinámicas se refiere, una de las más serias objeciones a dicho modelo [53] se debe a la naturaleza multinivel de moléculas quirales reales. Aun así, tal y como se ha demostrado recientemente [54], es posible utilizar un modelo de dos estados *efectivos* en el que la influencia del resto de niveles puede ser tenida en cuenta en los elementos de matriz del subespacio bidimensional que actúa sobre los dos enantiómeros. De esta forma, en lo que sigue nos restringiremos a la aplicación de un modelo de dos estados, añadiendo al mismo más ingredientes a medida que aumente la complejidad del problema que se quiera tratar.

Podemos describir una molécula quiral aislada como un sistema de dos estados (TLS, del inglés, *two–level system*), descrito por el Hamiltoniano

$$\hat{H} = \delta\hat{\sigma}_x + \epsilon\hat{\sigma}_z, \tag{3.13}$$

donde $\sigma_{x,z}$ son las matrices de Pauli. Como se ha dicho anteriormente, el TLS aislado puede verse como si proviniera, considerando la aproximación de Born–Oppenheimer, de un doble pozo asimétrico. A partir de los autoestados del Hamiltoniano $\hat{H}$, $|1\rangle$ y $|2\rangle$, los estados quirales, $|L\rangle$ y $|R\rangle$, pueden expresarse mediante una rotación de ángulo θ de los autoestados, donde $\tan 2\theta = \delta/\epsilon$, donde $\langle L|\hat{H}|R\rangle = -\delta$ (con $\delta > 0$) describe el efecto túnel entre ambos pozos y $2\epsilon = \langle L|\hat{H}|L\rangle - \langle R|\hat{H}|R\rangle$ (ϵ puede tomar valores positivos o negativos) representa la asimetría debida a la violación de la paridad.

Si desarrollamos la función de onda en la base quiral, $|\Psi(t)\rangle = a_L(t)|L\rangle + a_R(t)|R\rangle$, la dinámica de estereomutación entre enantiómeros vendrá completamente determinada por la ecuación de Schrödinger dependiente del tiempo ($\hbar = 1$)

$$i\partial_t \begin{pmatrix} a_L \\ a_R \end{pmatrix} = \begin{pmatrix} \epsilon & \delta \\ \delta & -\epsilon \end{pmatrix} \begin{pmatrix} a_L \\ a_R \end{pmatrix}. \tag{3.14}$$

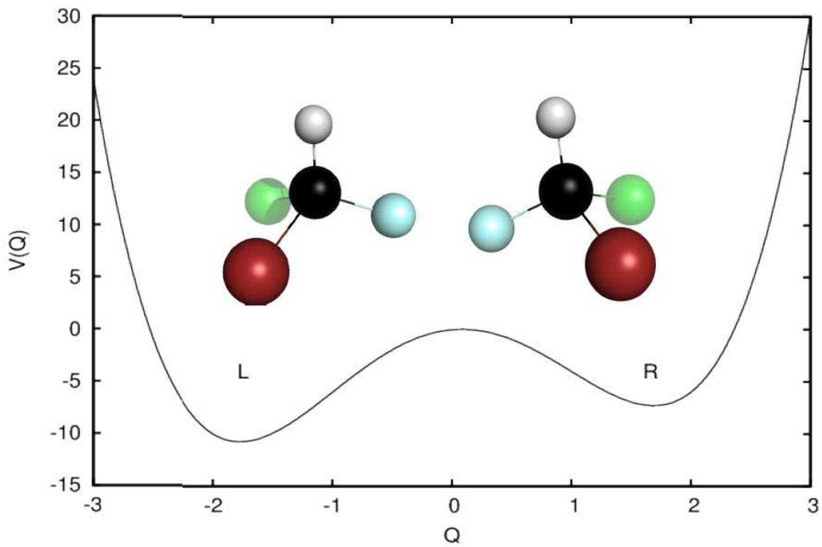

Figura 3.1: Superficie de energía potencial de una molécula quiral en la aproximación de Born–Oppenheimer. La asimetría se debe a la violación de la paridad.

Debido al carácter lineal de dichas ecuaciones (acopladas), es sencillo obtener su solución:

$$\begin{aligned} a_L(t) &= a_L^0 \cos \Delta t - \frac{i}{\Delta}\left(a_L^0 \epsilon + a_R^0 \delta\right) \sin \Delta t \\ a_R(t) &= a_R^0 \cos \Delta t + \frac{i}{\Delta}\left(a_R^0 \epsilon - a_L^0 \delta\right) \sin \Delta t, \end{aligned} \tag{3.15}$$

donde $\Delta \equiv \sqrt{\delta^2 + \epsilon^2}$ y $a^0_{i=L,R}$ denotan las condiciones iniciales.

Aun siendo un modelo sencillo, cuando se complementa con los valores de δ y ϵ calculados de manera *ab initio* [27] teniendo en cuenta todos los posibles grados de libertad de la molécula objeto de estudio, el modelo del TLS resulta ser una valiosa herramienta para poder diseñar (al menos de forma teórica) experimentos ópticos con los que poder detectar las pequeñas diferencias de energía electrodébil entre enantiómeros [55–57].

3.0.5. Modelo Meyer–Miller–Stock–Thoss

Otra formulación del TLS, comunmente empleada en el estudio de dinámica cuántica no adibática en Física Molecular, es la debida a Meyer y Miller [58, 59], posteriormente refinada por Stock y Thoss [60]. Se basa en la introducción de variables canónicas complejas, logrando así una equivalencia entre mecánica clásica y cuántica [61, 62]. En particular, nosotros hemos considerado las siguientes variables acción–ángulo [63]

$$\begin{aligned} z(t) &\equiv |a_R(t)|^2 - |a_L(t)|^2 \\ \Phi(t) &\equiv \phi_R(t) - \phi_L(t), \end{aligned} \tag{3.16}$$

donde $a_j = |a_j|e^{i\phi_j}$, como las *naturales* con las que describir el TLS. Esto se debe, principalmente, a que la diferencia de poblaciones, $z(t)$, es una medida directa de la actividad óptica electrodébil [55, 64, 65].

Utilizando estas variables, se obtienen las siguientes ecuaciones, que son completamente equivalentes a las de la Ec. (3.14)

$$\begin{aligned} \dot{z} &= -\sqrt{1-z^2}\sin\Phi \\ \dot{\Phi} &= \frac{z}{\sqrt{1-z^2}}\cos\Phi + \frac{\epsilon}{\delta}, \end{aligned} \tag{3.17}$$

donde, por simplicidad, el tiempo se ha escalado como $t \to 2\delta t$.

Es interesante notar que dicho par de ecuaciones puede verse como un par de ecuaciones de Hamilton (o Heisenberg), según $\dot{z} = -\partial_\Phi H_0$ y $\dot{\Phi} = \partial_z H_0$ (o bien asumiendo $[z, \Phi] = i$), siendo H_0 la función Hamiltoniana

$$H_0 = -\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z, \tag{3.18}$$

que satisface $2\delta H_0 = \langle\Psi|H|\Psi\rangle$, en acuerdo con la teoría general presentada en [61].

El par de ecuaciones dado en la Ec. (3.17) puede resolverse y obtener una expresión analítica para la actividad óptica [63]. En particular, en la Fig. (3.2) pueden observarse los *quantum beats* predichos por Harris y Stodolsky [51]. Nótese que las oscilaciones serán simétricas o asimétricas según se tenga $\delta \gg \epsilon$ o $\delta \ll \epsilon$.

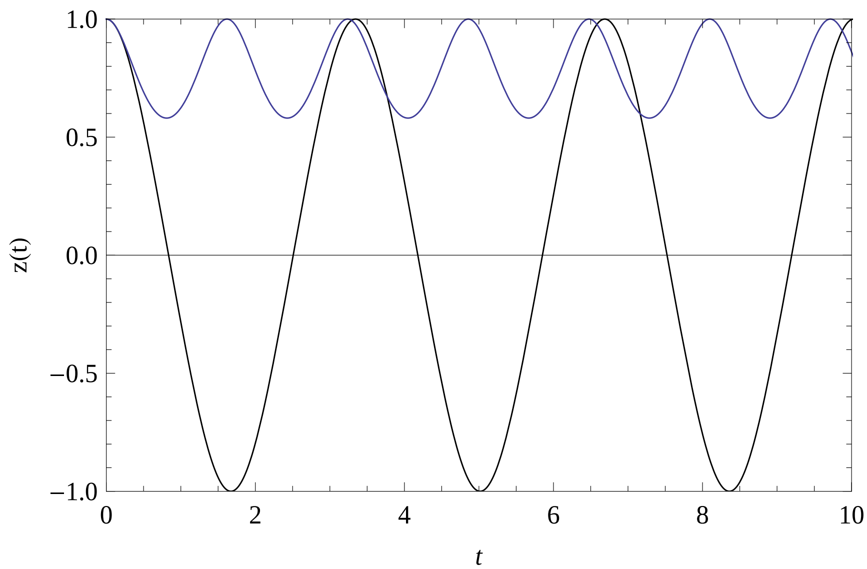

Figura 3.2: *Quantum beating* en la actividad óptica electrodébil.

Una generalización de dicho modelo, incluyendo interacciones intermoleculares y efectos disipativos, ha sido considerado en [63], tal y como se mostrará en apartados subsiguientes.

3.0.6. Interacción neutrino (WIMP)–molécula quiral

Habiendo descendido desde la teoría electrodébil hasta un modelo sencillo que incluye efectos de violación de paridad en moléculas quirales, como es el TLS en cualquiera de las representaciones empleadas, en esta sección comentaremos brevemente el modelo empleado en esta tesis para calcular diferencias de energía entre enantiómeros moleculares cuando interaccionan, bien con el mar de neutrinos cosmológicos, o bien con los WIMPS, partículas fermiónicas quirales que son cadidatos a materia oscura fría no bariónica.

El flujo isotrópicamente distribuido de neutrinos cosmológicos, predicho por la teoría del Big–Bang, es una reliquia de los neutrinos que se originaron en el Universo temprano, desacoplándose de otras partículas aproximadamente un segundo después de la gran explosión [66]. La interacción neutrino–electrón *via* procesos débiles que violan la paridad fue primeramente estudiada por Stodolsky [67] con objeto de poder detectar el mar de neutrinos en el laboratorio y posteriormente por otros autores [39, 68] (la existencia de dicho mar todavía no ha sido confirmada). Concretamente, se conoce con el nombre de *efecto Stodolsky* al desdoblamiento en energía de los dos estados de helicidad del electrón cuando interacciona con el baño de neutrinos, siendo dicho desdoblamiento proporcional a la diferencia de las densidades de neutrinos y antinuetrinos. Dicho efecto se puede describir a partir de un Hamiltoniano similar al presentado en la Ec. (3.4), teniendo en cuenta que ahora estamos tratando con neutrinos en vez de con nucleones.

En este sentido, notemos que aparecen dos nuevas e importantes magnitudes

$$\begin{aligned} \bar{\nu}\gamma^{\mu}\nu &\sim n_{\nu} - n_{\bar{\nu}} \\ \bar{\nu}\gamma^{\mu}\gamma^{5}\nu &\sim n_{\nu_l} - n_{\bar{\nu}_r}, \end{aligned} \tag{3.19}$$

que dan lugar al desdoblamiento de los dos estados de helicidad del electrón (la primera ecuación hace referencia a neutrinos de Dirac y la segunda a neutrinos de Majorana) obteniéndose

$$\Delta E_{\nu} \sim G_F(n_{\nu} - n_{\bar{\nu}}) \sum_i \langle L|\mathbf{p}_i \cdot \mathbf{s}_i|L\rangle. \tag{3.20}$$

Podemos estimar la helicidad de los electrones externos de una molécula quiral, dada por $\langle L|\mathbf{p}\cdot\mathbf{s}|L\rangle$ mediante un modelo sencillo desarrollado en [69]. Consideremos una configuración nuclear axial a lo largo del eje z con periodicidad a, de tal forma que un electrón puede ser descrito por ($\hbar = 1$) $|K,p\rangle = \phi(\rho)e^{iK\chi}e^{ikz}$, donde ρ es la coordenada radial, χ es el ángulo alrededor de z, K es el número cuántico asociado al momento angular L_z y $k = (2\pi a)/p$, con $P = 0, \pm1, \pm2, ...$, son los auotvalores del momento P_z. El estado fundamental lo denotamos $|0,0\rangle$. Si ahora consideramos un potential perturbativo helicoidal *a izquierdas* de la forma $V_L = V_0 \exp[i(2\pi z/a) - \chi] + c.c$, el estado $|0,0\rangle$ se conectará con $|\pm1,\mp1\rangle$ de tal forma que, aprimer orden en teoría de perturbaciones, el nuevo estado electrónico vendrá dado por $|L\rangle = c_0|0,0\rangle + c_1|1,-1\rangle + c_2|-1,1\rangle$ con $c_1^2 = c_2^2 \equiv C$. Esto es, el electrón sigue una hélice viajando a lo largo de la dirección z con momento P_z y momento angular

L_z con una helicidad dada por

$$\langle L|L_zP_z|L\rangle = -\frac{4C\pi}{a.} \tag{3.21}$$

De manera anloga puede demostrarse que, si introducimos un potential helicoidad *a derechas*, $V_R = V_0 \exp[i(2\pi z/a)+\chi]+c.c$, el estado electrónico perturbado será $|R\rangle = c_0|0,0\rangle + c_1'|1,-1\rangle + c_2'|-1,-1\rangle$, resultando tener helicidad opuesta,

$$\langle R|L_zP_z|R\rangle = -\langle L|L_zP_z|L\rangle. \tag{3.22}$$

El espín del electrón también puede tenerse en cuenta reemplazando L_z por $J_z = L_z + S_z$. Además, notemos que, aunque en un modelo relista de molécula quiral los electrones no serán, en general, autoestados de la helicidad, su valor medio tendrá signo contrario para enantiómeros opuestos.

Pues bien, insertando el valor de la helicidad electrónica en la Ec. (3.20) junto con la cota superior para la asimetría $n_\nu - n_{\bar{\nu}} \sim 1000$ cm^{-3} [39, 70], se obtiene $\Delta E_\nu \sim 10^{-21}$ eV. Por lo tanto, no es descabellado concluir que el efecto de los neutrinos cosmológicos sobre la homoquiralidad molecular puede ser del mismo orden que el proporcionado por la interacción débil electrón–núcleo en algunas moléculas quirales.

El tratamiento teórico considerado para estimar el desdoblamiento de los dos estados quirales moleculares en caso de interaccionar con WIMPs es similar al anterior, exceptuando algunos puntos técnicos referentes a cómo poder acotar tanto el valor de los acoplamientos electrodébiles WIMP–electrón como su masa. El procedimiento detallado se expone en la Ref. [37].

4

Sobre la posible detección de violación de la paridad en moléculas quirales. Experimentos ópticos

Según la prestigiosa revista *Nature*, la detección de efectos electrodébiles en moléculas quirales, en concreto la PVED, definida en la Ec. (2.6), es uno de los cinco experimentos tan difíciles de llevar a cabo como encontrar el bosón de Higgs [71]. Las principales propuestas experimentales que se encuentran en la literatura son:

- Medidas espectroscópicas de observables quirales en moléculas aquirales. Por ejemplo, actividad óptica debido a la violación de la paridad [64, 65, 72, 73].

- Medidas de la dependencia temporal de la actividad óptica electrodébil en moléculas en las que $\epsilon \simeq \delta$ [51, 55, 57]. También hay algunas prouestas que hacen extensivo este esquema al caso de estados vibracionalmente excitados [53].

- Medidas espectroscópicas de ultra–alta resolución de la posible diferencia de frecuencias de diversas líneas espectrales de diferentes enantiómeros (infrarroja, microondas, visible, resonancia magnética nuclear, rayos γ) [27, 31, 48–50, 74–79].

- Experimentos espectroscópicos que conectan los correspondientes niveles de los dos enantiómeros mediante transiciones radiativas hacia un estado aquiral intermedio de paridad bien definida. Este experimento puede llevarse a cabo tanto en el dominio de frecuencias como en el temporal [52, 53, 72].

Nosotros hemos centrado nuestra atención en la medida de la dependencia temporal de la actividad óptica electrodébil en moléculas quirales, siguiendo las ideas pioneras de Harris y Stodolsky [51] y de MacDermott y Hegström [64]. Hemos propuesto varios experimentos con los cuales, en principio, podría determinarse, de manera indirecta, la PVED. A continuación pasamos a enumerarlos y explicarlos muy brevemente.

4.0.7. Temperatura cero

Se ha propuesto un experimento mediante el cual se pudiera medir la PVED en moléculas quirales modificando la dinámica del TLS mediante la aplicación de un campo quiral externo, en particular, utilizando LCP. La diferencia de energías electrodébil entre los dos enantiómeros puede ser compensada por la influencia quiral externa, resultando en cambios apreciables en la actividad óptica oscilante en moléculas en las que $\epsilon \sim \delta$. De esta forma, a partir de la observación de los cambios en el promedio temporal de dicha actividad óptica de una muestra pura (esto es, totalmente quiral), en la que los efectos del entorno han sido minimizados, se podría extraer el valor de la PVED [55].

La idea se basa en modificar el ángulo de mezcla, $\tan 2\theta = \frac{\delta}{\epsilon}$ mediante la aplicación de LCP. En dicho caso, se obtiene trivialmente que, si el promedio temporal de la quiralidad del campo es no nulo, podemos hace la sustitución $\epsilon \to \epsilon + \tilde{\epsilon}$, donde $\tilde{\epsilon}$ es la diferencia de energías entre los dos enantiómeros al interaccionar con LCP mediante el Hamiltoniano

$$H = \boldsymbol{\mu} \cdot \mathbf{E}^{\pm}(t) - \mathbf{m} \cdot \mathbf{B}^{\pm}(t), \tag{4.1}$$

donde $\boldsymbol{\mu}$ y $\mathbf{m}$ son los operadores de momento dipolar eléctrico y magnético, respectivamente, y $\mathbf{E}^{\pm}(t)$ y $\mathbf{B}^{\pm}(t)$ son campos eléctricos y magnéticos circularmente polarizados, $\pm$ señalando la quiralidad (helicidad) de la polarización.
Dicha diferencia de energías viene dada por [80]

$$\tilde{\epsilon} = \frac{8}{3} E B \omega \frac{R_{n0}}{\omega_{n0}^2 - \omega^2}, \tag{4.2}$$

donde ω_{n0} es la frecuencia de resonancia más cercana a la frecuencia incidente, ω, $R_{n0} = \mathrm{Im}(\mu_{n0} \cdot \mathbf{m}_{n0})$. Además, como el período de la radiación electromagnética es mucho más corto que el tiempo de oscilación molecular, se ha hecho un promedio temporal.

Si aproximamos los correspondientes elementos de matriz dipolares eléctricos y magnéticos por ea_0 (a_0 es el radio de Bohr) y por el magnetón de Bohr, $e/2mc$, obtenemos que, incidiendo con luz roja y utilizando que $\omega^2/(\omega_{n0}^2 - \omega^2) \simeq 1$ [81], podríamos compensar una PVED del orden de $10^{-16} - 10^{-18}$ eV utilizando un campo eléctrico de $E \simeq 200 - 2000$ V m^{-1} [55]. Por lo tanto, utilizando dicho campo eléctrico, podríamos observar cambios apreciables en la actividad óptica de una muestra pura de moléculas quirales, siempre y cuando la PVED sea no nula. En particular, dicha actividad óptica cambia de signo cuando $\epsilon = -\tilde{\epsilon}$, lo cual podría controlarse experimentalmente con ayuda del citado campo eléctrico.

Es interesante notar que el mecanismo propuesto en [55] no es otra cosa que un mecanismo resonante puesto que se busca un campo eléctrico tal que el $\epsilon = -\tilde{\epsilon}$. En dicho caso, el ángulo de mezcla sería $\pi/4$ y la probabilida de oscilación entre estados $|L\rangle$ y $|R\rangle$ sería máxima. A partir de dicha observación, se ha mostrado que existe una analogía entre dicho mecanismo y la resonancia MSW en las oscilaciones entre neutrinos de dos sabores [82–84], tal y como se muestra en [85].

4.0.8. Temperatura finita

También hemos ampliado la definición de la activida óptica electrodébil, dentro del formalismo de Harris-Stodolsky, para el caso de temperaturas finitas [56]. En particular, se ha generalizado un teorema de de Gennes [86] teniendo en cuenta tanto el efecto túnel entre enantiómeros como la diferencia de energía electrodébil existente entre ambos. Concretamente, se puede demostrar que el promedio térmico de cualquier observable pseudoescalar X (esto es, representable mediante σ_z en la base quiral) viene dado por [56]

$$|\langle X\rangle_\beta| = \cos 2\theta \tanh \beta\Delta, \tag{4.3}$$

donde $\Delta = \sqrt{\delta^2 + \epsilon^2}$ y $\beta = (k_B T)^{-1}$ siendo k_B la constante de Boltzmann.

A partir de la localización del punto de inflexión de dicho observable pseudoescalar, se ha introducido el concepto de temperatura crítica, T_c, como aquella que separa la región en la que los efectos térmicos enmascaran la dinámica quiral interna, regida por la relación entre ϵ y δ. Utilizando dicho concepto, hemos propuesto un experimento de rotación óptica para detectar la PVED. En particular, se ha mostrado como, para algunas moléculas y a temperaturas suficientemente bajas (del orden del mK o incluso del K), la competición entre la violación de la paridad, el efecto túnel y los efectos térmicos, dan lugar a un exceso enantiomérico en el equilibrio termodinámico, dado por

$$n_L - n_R = \frac{\epsilon^2}{\sqrt{\epsilon^2 + \delta^2}} \tanh \beta\Delta. \tag{4.4}$$

Dicho exceso es capaz de producir una rotación óptica medible utilizando polarímetros de ultra–alta precisión [57].

4.0.9. Condensación de Bose–Einstein de moléculas quirales

Como una ruta alternativa para detectar la PVED, hemos estudiado un modelo simplificado de condensación de Bose–Einstein de moléculas quirales sin interacción [87]. La existencia de violación de la paridad da lugar a una actividad óptica no nula para la fase condensada y a una temperatura subcrítica en la capacidad calorífica.

En particular, hemos hecho extensivo el teorema de de Gennes a cualquier tipo de estadística: Maxwell–Boltzmann, Fermi–Dirac o Bose–Einstein, obteniendo

$$|\langle X\rangle_\beta|_= \tanh \beta\Delta \left[1 + p \cosh(\beta\mu) \operatorname{sech}(\beta\Delta)\right], \tag{4.5}$$

donde μ es el potencial químico y $p = 0, +1, -1$ para las estadísticas de Maxwell–

Boltzmann, Fermi–Dirac y Bose–Einstein, respectivamente.

Para este sencillo modelo, la temperatura crítica se puede definir como

$$T_* = \frac{2\Delta}{k_B \ln(1 + \frac{1}{N})}, \tag{4.6}$$

lo cual implica una actividad óptica proporcional a

$$N_L - N_R = \frac{\epsilon}{\Delta} N \left(1 - \frac{2e^{2\beta_* \Delta} - 1}{e^{2\beta\Delta} - 1}\right) \tag{4.7}$$

y una capacidad calorífica, también dependiente de la PVED, que se escribe como

$$C_v = 4k_B(\beta\Delta)^2 \frac{2e^{2\beta_*\Delta}}{2e^{2\beta\Delta} - 1}. \tag{4.8}$$

Es interesante notar que esta capacidad calorífica presenta un máximo para la llamada temperatura subcrítica, T_{sc}, la cual no refleja otra cosa que la anomalía de Schottky debido a la saturación de niveles de energía del sistema. Por lo tanto, de nuevo seleccionando la molécula apropiada y conociendo su desdoblamiento por efecto túnel, podrían deducirse valores para la PVED tanto a partir de experimentos de rotación óptica como explorando la capacidad calorífica de condensados moleculares a temperaturas suficientemente bajas [87].

4.0.10. Resonancia Estocástica

De nuevo motivados por entender las diversas manifestaciones de la violación de la paridad en moléculas quirales, hemos estudiado el fenómeno de *resonancia estocástica cuántica* (RE) en la actividad óptica electrodébil bajo condiciones de baja fricción y en el régimen puramente cuántico. Muy brevemente, el fenónemo de la RE consiste en lo siguiente. Apliquemos una fuerza periódica débil a una partícula que se mueve en el seno de un doble pozo de potencial, de tal forma que los mínimos suben y bajan alternadamente como indica la Fig. (4.1). Aunque dicha fuerza es demasiado débil como para que la partícula se mueva peródicamente hacia ambos lados de la barrera de potencial, podemos sincronizar el período de la fuerza externa con los saltos que el ruido induce en la partícula. La característica general de un sistema que muestra RS es el aumento de la sensibilidad frente a pequeñas perturbaciones cuando se añade la dosis apropiada de ruido. En resumen, los ingredientes básicos de la RS son: la existencia de un umbral, una fuente de ruido y un *imput* en forma de fuerza débil.

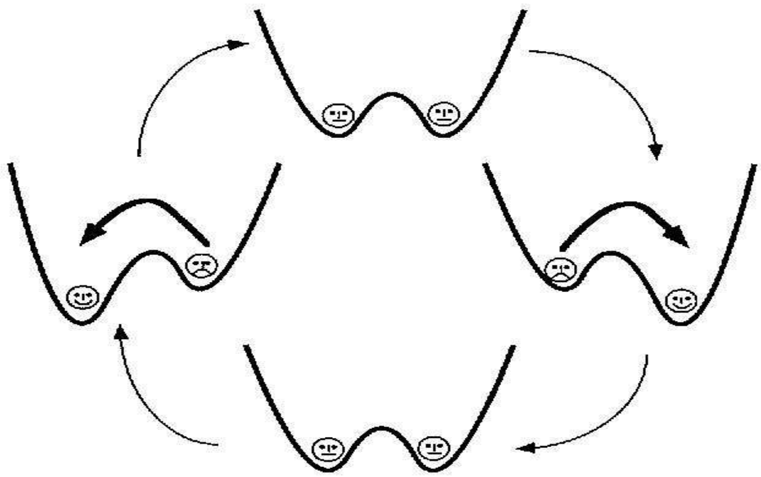

Figura 4.1: Representación esquemática del fenómeno de la resonancia estocástica (tomado de [88])

En el caso que nos ocupa, se ha partido de un Hamiltoniano tipo *spin–boson* que describe una molécula quiral (modelo de Harris–Stodolsky) al que se ha añadido un potencial externo cuya forma depende del tiempo sinusoidalmente,

$$H = \delta\sigma_x + (\epsilon + \tilde{\epsilon}\cos\Omega t)\sigma_z + \frac{1}{2}\sum_j(\frac{p_j^2}{m} + m_j\omega_j^2 x_j^2 - c_j x_j a\sigma_z), \qquad (4.9)$$

donde $\tilde{\epsilon}\cos\Omega t$ es la energía de interacción de la molécula con el campo externo, que oscila con frecuencia Ω, x_j son las coordenadas de los osciladores del baño, cuya frecuencia es ω_j, a es la distancia entre los dos mínimos del pozo de potencial y c_j son constantes de acoplamiento.

Para tiempos largos comparados con la dinámica transitoria, el valor asintótico de la actividad óptica, que será proporcional a $\langle P(t)\rangle \equiv \langle n_L - n_R\rangle$, donde el promedio se realiza sobre los grados de libertad del baño, se expresa como [88]

$$P_{as}(t) = \sum_{-\infty}^{\infty} P^{(m)}(\Omega\epsilon)e^{-im\Omega t}, \tag{4.10}$$

Teniendo en cuenta que la amplificación espectral de la m–ésima frecuancia se define como $|P^{(m)}/\epsilon|^2$ y que, en el régimen de respuesta lineal, sólo las contribuciones $m = 0, \pm 1$ son importantes, se llega a que la amplificación espectral, $|P^1/\epsilon|$, presenta un máximo a una temperatura T_{sr}, tal que [89]

$$\beta_{sr}\epsilon \tanh \beta_{sr}\epsilon = 1, \tag{4.11}$$

lo cual está de acuerdo con el hecho de que la temperatura a la que aparece el fenómeno de RS es del orden de la asimetría estática [88]. Es interesante resaltar que la RE cuántica en moléculas quirales aparece únicamente en presencia de la PVED, independientemente de la probabilidad de la transición túnel entre enantiómeros, lo cual podría ser susceptible de detección experimental.

5

Espectroscopía de ultra–alta resolución en moléculas quirales como herramienta para estudiar violación de la paridad en gravitación

A partir de la predicción y el subsiguiente descubrimiento de la violación de la paridad en las interacciones débiles [90, 91], las relaciones existentes entre la ruptura de simetría y el extremadamente pequeño valor de la interacción, llevó a Leitner y Okubo [92] a preguntarse si la gravitación podría incorporar dicha ruptura de simetría. Posteriormente, Hari Dass introdujo fenomenológicamente un potencial gravitatorio en el que se incluían varios términos que se acoplaban con el espín de una partícula de prueba, dando lugar a la violación de PT CP y CT. Dicho potencial se puede expresar como [93]

$$U(r) = \alpha_1 \frac{GM\mathbf{s}\cdot\mathbf{r}}{r^3} + \alpha_2 \frac{GM\mathbf{s}\cdot\mathbf{v}}{r^2} + \alpha_3 \frac{GM\mathbf{s}\times(\mathbf{r}\cdot\mathbf{v})}{r^3}, \tag{5.1}$$

donde M es la masa del objeto gravitante, α_1, α_2 y α_3 son constantes adimensionales que describen, suponiendo conservación de CPT, violación de PT CP y CT, respectivamente (notemos que la masa de la partícula de prueba, m, viene incorporada en la definición de las constantes α_i).

El problema radica en que, hasta el momento, no se tiene constancia del valor exacto de las constantes de acoplo espín–gravitatorias, exceptuando algunas cotas, obtenidas bien de manera directa, o bien de manera indirecta, a partir de observaciones astrofísicas o mediante experimentos relizados con materiales polarizados en balanzas de torsión [94–104]. Por lo tanto, no sabemos en qué medida la gravitación incluye, por ejemplo, violación de la paridad de manera natural, tal y como predicen algunas generalizaciones de la Relatividad General en las que se incluye torsión [105].

En este sentido, hemos visto aquí la posibilidad de restringir el valor de la costante α_2, que implica violación de la paridad en la interacción gravitatoria. Es decir, hemos tenido en cuenta que dicha interacción da lugar a una diferencia de energías entre enantiómeros de una molécula quiral, según la expresión [106]

$$\Delta E^{PV}_{\alpha_2} = \alpha_2 \frac{GM}{r^2 m_e} \sum_i \chi_i, \tag{5.2}$$

donde χ_i es la helicidad del i–ésimo electrón molecular [107].

Ahora bien, teniendo en cuenta que todavía no se ha detectado experimentalmente *ninguna* diferencia de energías entre enantiómeros moleculares opuestos con una resolución experimental de 10^{-14} eV utilizando los enantiómeros de CHBrClF [76], podemos concluir que $\Delta E^{PV}_{\alpha_2} \leq 10^{-14}$ eV. Suponiendo que la principal interacción espín–gravitatoria se debe a la interacción entre la Tierra y los electrones de dicha molécula, inferimos la cota [106]

$$\alpha_2 \leq 10^{17}, \tag{5.3}$$

la cual mejora, sustancialmente, todas las cotas obtenidas anteriormente mediante observaciones astrofísicas (notemos, sin embargo, que aquellas obtenidas tanto mediante experimentos con iones atrapados [103], como con balanzas de torsión [104], siguen siendo las más restrictivas).

6

Interacción entre moléculas quirales. Efectos disipativos

La interacción de una molécula quiral con entorno se considera la principal fuente de pérdida de coherencia de los estados de paridad bien definida (que son superposición de los estados quirales) y también el origen de la estabilización de los estados quirales localizados. Utilizando el modelo de Harris–Stodolsky se encontró que, si la frecuencia de colisión en un gas de moléculas quirales es suficiéntemente alta comparada con la frecuencia de túnel entre $|L\rangle$ y $|R\rangle$, la coherencia de dicho proceso se pierde al tiempo que la evolución hacia el estado racémico puede ser considerablemente lenta [108–112]. Recientemente, Trost y Hornberger [113] han identificado, utilizando técnicas de *scattering* molecular, el mecanismo colisional dominante en el proceso de decoherencia, lo cual explica la estabilización de las moléculas quirales debido a la interacción con un gas de fondo.

El papel de las interacciones moleculares en la localización y estabilización de estados quirales moleculares es un tema ampliamente estudiado [114–120]. En particular, Vardi tuvo en cuenta el efecto de las interacciones homoquirales y heteroquirales mediante una aproximación de campo medio, obteniendo un par de ecuaciones acopladas no lineales para las amplitudes de los estados quirales [121]. El principal resultado de dicho trabajo fue la obtención del fenómeno de *auto–atrapamiento* en uno de los estados quirales, siempre y cuando la diferencia de energías hetero–homo fuera suficientemente grande. Aquí prescindiremos de la interacción débil por ser mucho más pequeña que las otras interacciones.

6.0.11. Formalismo de la matriz densidad. Modelo Harris-Stodolsky

En este marco, hemos estudiado el efecto de decoherencia por colisiones en el modelo de Vardi, partiendo de la aproximación de Harris–Stodolsky para la molécula quiral [122].

Consideremos el efecto de las interacciones intermoleculares teniendo en cuenta que cada molécula está sujeta a un campo medio resultante de las restantes moléculas. Supongamos que dicho campo tiene contribuciones homo y heteroquirales. En la base quiral, los elementos de matriz del Hamiltoniano correspondiente se escriben como

$$\begin{aligned} H_{LL} &= \epsilon + U_{hom}|a_L|^2 + U_{het}|a_R|^2 \\ H_{RR} &= -\epsilon + U_{hom}|a_R|^2 + U_{het}|a_L|^2, \end{aligned} \tag{6.1}$$

donde U_{hom} and U_{het} son las intensidades de la interacción homoquiral (L–L,R–R) y heteroquiral (L–R), respectivamente.

Hemos usado el formalismo de la matriz densidad para estudiar la evolución del estado superposición $|\Psi\rangle = a_L|L\rangle + a_R|R\rangle$ sujeto a las interacciones anteriormente mencionadas. Como sólo estamos interesados en la dinámica del sistema molecular de dos estados, utilizamos la ecuación maestra para la matriz densidad reducida del estado molecular (es decir, se supone realizada la traza sobre las variables del baño). Asumiendo un acoplamiento débil molécula–entorno y, en la aproximación de Markov (el sistema no tiene memoria), la ecuación que tenemos que resolver es

$$\frac{d\rho_{ij}}{dt} = -\frac{i}{\hbar}[H,\rho]_{ij} - \gamma_{ij}\rho_{ij}, \tag{6.2}$$

donde $i, j = L, R$ y las constantes γ_{ij}, que describen los efectos colisionales, han sido introducidas fenomenológicamente.

El principal resultado que hemos obtenido [122], analizando tanto la diferencia de poblaciones como las coherencias, ha sido que el mecanismo de decoherencia considerado conduce, inexorablemente, a un estado final racémico, independientemente del valor de la interacciones intermoleculares. Por lo tanto, podemos decir que la decoherencia colisional tiende a destruir el auto–atrapamiento de Vardi anteriormente mencionado.

En caso que el tiempo de decoherencia sea mucho mayor que el tiempo de transición túnel, hemos encontrado que la estabilización molecular puede verse incrementada, e incluso dominada, por la contribución de las interacciones intermoleculares. En este caso, el tiempo de estabilización es, en la mayoría de las situaciones, varios órdenes de magnitud superior al tiempo de la transición túnel. Por el contrario, cuando el tiempo de decoherencia es menor que el de dicha transición, el efecto estabilizador de la interacciones intermoleculares se ve disminuido por la decoherencia colisional. Aun así se obtiene estabilización para tiempos superiores al de la transición túnel [122].

6.0.12. Formalismo de Langevin. Modelo Meyer–Miller–Stock–Thoss

Tal y como se discutió en capítulos anteriores, un formalismo alternativo para representar una molécula quiral viene dado por el Hamiltoniano Meyer–Miller–Stock–Thoss [58–60]. Teniendo en cuenta que z y Φ, definidas en la Ec. (3.16), son un par de coordenadas canónicas equivalentes a un momento y posición generalizados, respectivamente, podemos introducir interacciones con el entorno de tipo Caldeira–Leggett [123]. De esta forma, podemos descomponer el Hamiltoniano total como suma de Hamiltonianos que describen a la molécula quiral (según el modelo Meyer–Miller–Stock–Thoss), al entorno (tomado como conjunto de osciladores armónicos) y a la interacción entre ambos (interacción bilineal, según [123]),

$$H_{tot} = H_0 + \frac{1}{2}\sum_i \left(\Lambda_i p_i^2 + \Lambda_i^{-1} x_i^2 \omega_i^2\right) - \Phi \sum_i c_i x_i + \sum_i \Phi^2 c_i^2 \Lambda_i, \tag{6.3}$$

donde

$$H_0 = -\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta} z + \frac{\kappa}{4\delta} z^2 \tag{6.4}$$

es el Hamiltoniano de la molécula quiral teniendo en cuenta las interacciones intermoleculares, $\kappa = U_{het} - U_{hom}$ y Λ_i, ω_i, x_i y c_i son las masas, frecuencias de oscilación, posición y las constantes de acoplamiento del i–ésimo oscilador del baño con la molécula, respectivamente.

Si eliminamos los grados de libertad del baño, obtenemos las ecuaciones de evolución [63]

$$\begin{aligned} \dot{z} &= -\sqrt{1-z^2}\sin\Phi \\ &- \int_0^t \gamma(t-t')\Phi(t')\dot{\Phi}(t')\,dt' + \xi(t) \\ \dot{\Phi} &= -\frac{\kappa}{2\delta}z + \frac{z}{\sqrt{1-z^2}}\cos\Phi + \frac{\epsilon}{\delta} \end{aligned} \tag{6.5}$$

donde

$$\gamma(t) = \sum_i \Lambda_i c_i^2 \cos\omega_i(t-t') \tag{6.6}$$

representa el término disipativo (fricción) y

$$\xi(t) = \sum_i c_i\Lambda_i\left(x_i(0)\cos\omega_i t + p_i(0)\sin\omega_i t\right) - c_i^2\Lambda_i\Phi(0)\cos\omega_i t \tag{6.7}$$

es una fuerza estocástica (ruido).

Si consideramos disipación de tipo Ohmico, la fricción se expresa como $\gamma(t) = 2\gamma\delta(t)$, dando lugar a un término del tipo $-\gamma\dot{\Phi}$ en la Ec. (6.5) [63]. Además, como sólo queremos estudiar dinámica disipativa (esto es, a temperatura cero), despreciamos los términos de ruido, obteniendo

$$\begin{aligned} \dot{z} &= -\sqrt{1-z^2}\sin\Phi - \gamma\dot{\Phi} \\ \dot{\Phi} &= -\frac{\kappa}{2\delta}z + \frac{z}{\sqrt{1-z^2}}\cos\Phi + \frac{\epsilon}{\delta}. \end{aligned} \tag{6.8}$$

Es interesante notar que el término de fricción es proporcional a la velocidad generalizada, tal y como suele introducirse de manera fenomonológica en algunos modelos sencillos de disipación [124].

Como puede verse en [63], la principal diferencia entre este tratamiento tipo Langevin y el anterior, basado en la matriz densidad, es la ausencia de racemización que se obtiene al resolver las Ecs. (6.8).

7

Conclusiones

Como principales resultados de esta tesis cabe mencionar lo siguiente:

- La interacción neutrino–molécula quiral da lugar a una diferencia energética entre los dos enantiómeros inferior a 10^{-21} eV en el caso de neutrinos cosmológicos. Se ha estimado que dicha discriminación podría verse incrementada al considerar neutrinos provenientes de explosiones de supernova. En dicho caso, la mencionada diferencia energética podría alcanzar los 10^{-5} eV.

- Se ha descartado la materia oscura fría fermiónica como posible precursor de la homoquiralidad.

- Controlando la rotación óptica promediada en el tiempo mediante un láser convencional que produzca LCP y minimizando los efectos del entorno empleando haces moleculares diluidos, se ha propuesto un experimento para detectar la diferencia de energía electrodébil entre enantiómeros de D_2Se_2.

- Como consecuencia del anterior estudio, se ha establecido una analogía entre la actividad óptica oscilante y la resonancia MSW observada en neutrinos.

- El estudio termodinámico realizado ha permitido, mediante la generalización de un teorema de de Gennes, definir una temperatura crítica por debajo de la cual los procesos debidos a la violación de la paridad dominan sobre la racemización inducida por efectos térmicos. Los valores críticos tanto de la entropía como de la capacidad calorífica son constantes e independientes de la molécula quiral objeto de estudio.

- Como consecuencia del anterior estudio, se propone otro experimento (con H_2Se_2, H_2Te_2 y algunos isotopólogos) en el que, una vez se haya obtenido la diferencia enantiomérica deseada a bajas temperaturas, la supresión del efecto túnel permite mantener dicha diferencia en condiciones de trabajo del polarímetro.

- Se ha generalizado el anteriormente mencionado teorema a cualquier tipo de estadística. En particular, se ha estudiado un modelo simple de condensación de Bose–Einstein de moléculas quirales sin interacción, con especial énfasis en algunos efectos electrodébiles que aparecen en fase condensada como consecuencia de una anomalía tipo Schottky. Dicha anomalía da lugar tanto a la aparición de un condensado con actividad óptica como a una temperatura subcrítica en la capacidad calorífica que podrían ser susceptibles de detección experimental.

- Se ha predicho un fenómeno de resonancia estocástica a bajas temperaturas que sólo puede ocurrir si la diferencia de energías entre enantiómeros es distinta de cero. Dicho fenómeno proporciona una vía alternativa de detección de dicha diferencia energética.

- El hecho de no haberse detectado todavía ninguna diferencia energética electrodébil entre enantiómeros se ha utilizado para establecer cotas a una interacción gravitatoria que incluye violación de la paridad.

- Se ha estudiado la dinámica disipativa del proceso de transición túnel entre moléculas quirales incluyendo interacciones intermoleculares, con especial énfasis en los procesos de auto–atrapamiento y decoherencia, tanto colisional (que da lugar a racemización, aunque a veces en tiempos tan largos como años, en concordancia con otros trabajos) como debido a interacciones con un medio continuo (que no da lugar a racemización).

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EFFECT OF COSMOLOGICAL NEUTRINOS ON DISCRIMINATION BETWEEN THE TWO ENANTIOMERS OF A CHIRAL MOLECULE

PEDRO BARGUEÑO[1,*] and ISABEL GONZALO[2]
[1]*Instituto de Matemáticas y Física Fundamental, Consejo Superior de Investigaciones Científicas, Serrano 123, 28006-Madrid, Spain;* [2]*Departamento de Óptica, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040-Madrid, Spain*
*(*author for correspondence, e-mail: pbdr@imaff.cfmac.csic.es)*

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Abstract. In the framework of an extraterrestrial origin of biological homochirality, universal mechanisms are of particular interest. In this sense we consider the weak parity-violating neutrino-electron interaction through weak charged currents $W^{\pm}$ between the relic flux of cosmological neutrinos and the electrons of a chiral molecule. We use the known theoretical result of the split in energy of the two helicity states of an electron in the cosmic neutrino bath, due to weak charged currents. In the case that electrons of a chiral molecule are submitted to a helicoidal potential due to the nuclear conformation, these electrons have opposite helicities for the two enantiomers of the molecule and consequently the mentioned neutrino-electron interaction would produce a splitting in energy between the two enantiomers. An estimation of this energy for the case of a single electron yields a small value of the order of 10^{-26} eV. This value results amplified by the contribution of all the molecular electrons having helicity and other possible mechanisms.

Keywords: biological homochirality, cosmological neutrinos, electroweak interaction, molecular chiroselection

The origin of homochirality, that is, the almost exclusive one-handedness of the chiral molecules found in living systems (only L-amino acids and D-sugars), is one of the most fascinating problems, linked to the origin of life.

Several mechanisms have been proposed trying to explain it [see for example the review (Bonner, 1991) and contributions in Cline (1996)], involving chance, symmetry breaking by the action of electric, magnetic, gravitational fields, circularly polarized light and universal processes such as violation of parity in the weak interaction. All these mechanisms lead in general to a small discrimination between the two enantiomers of a chiral molecule, and would require large amplification factors (Mason, 1988; Kondepudi and Nelson, 1985), making it difficult to account for biological homochirality in Earth.

The discovery of an excess of L-amino acids in the Murchison meteorite (Cronin and Pizzarello, 1997), as well as the observation of infrared circular polarization from the Orion OMC-1 star-formation region (Bailey *et al.*, 1998), have reinforced the idea of an extraterrestrial origin of biological homochirality (Bonner, 1991; Bonner, 1992), although appropriate mechanisms involving polarized light in the necessary wavelength range are still speculative. In this framework, universal mechanisms such as weak parity-violating (P-odd) processes are of particular interest. In fact, electroweak interactions through neutral currents Z^0 between electrons and nuclei have been extensively studied. While the phenomenology of parity violating effects in atoms is now well established by experiment combined with highly accurate theoretical calculations (Bouchiat and Bouchiat, 1997), there exist no conclusive observations in molecules. It is accepted, however, that such interactions can lead to an energy difference between left-handed (L) and right-handed (R) enantiomers of a chiral molecule, estimated to be between 10^{-16} and 10^{-21} eV [see for example (Quack, 1989; Zanasi *et al.*, 1999; Laerdahl and Schwerdtfeger, 2000; Letokhov, 1975)].

In this paper we examine another universal process: cosmological neutrinos interacting with the electrons of chiral molecules. The isotropically distributed flux of cosmological neutrinos, predicted by the big-bang model, is a relic sea of neutrinos originated in the very early universe, decoupled from all other particles and from each other, approximately one second after the big bang. The interaction between neutrinos and electrons via a weak P-odd process mediated by charged currents $W^{\pm}$ was studied in relation to the detectability of the cosmological neutrino sea in a laboratory experiment. The first theoretical result (Stodolsky, 1975) was corroborated by others authors (Langacker *et al.*, 1983; Duda *et al.*, 2001) and consists in a split in energy of the two helicity states of an electron in the cosmic neutrino bath, the energy split being proportional to the difference between the densities of neutrinos and antineutrinos. This process could discriminate between the two enantiomers of a chiral molecule if their respective electrons have opposite helicity. Here, once we show that electrons of L and R enantiomers of some kind of chiral molecules may have opposite helicities, we estimate the corresponding difference in energy between the two enantiomers under the flux of cosmological neutrinos. As we shall show, such a difference in energy seems to be very small if some kind of amplification is not involved. In any case, we consider of interest this effect for research completeness of all possible universal mechanisms involved in chiroselection. Within this order of ideas, a speculation is made in a recent paper about a possible enantiomeric discrimination produced by supernova antineutrinos (Cline, 2004).

Let us consider the neutrino-electron interaction above mentioned, mediated by weak charged currents $W^{\pm}$, based on the effective Hamiltonian,

$$H(V, A) = \frac{G_F}{\sqrt{2}} \Sigma_{a=V,A} (\bar{\psi}_\nu \Gamma_a \psi_\nu)[\bar{\psi}_e \Gamma^a (g_a + g'_a \gamma_5) \psi_e] + H.c., \tag{1}$$

where $G_F \approx 10^{-5}/m_p^2$ (units$\hbar = c = 1$) is the weak coupling constant, $\Gamma^V = \gamma^\mu$, $\Gamma^A = \gamma^\mu \gamma^5$, γ^μ ($\mu = 0, 1, 2, 3$) are the Dirac matrices (regarded as a four vector), $\gamma^5 = i\gamma^0\gamma^1\gamma^2\gamma^3$, $\psi_{e(\nu)}$ is the electron (neutrino) spinor field, $\bar{\psi}_{e(\nu)} = \psi^+_{e(\nu)}\gamma^0$ is the adjoint spinor, and g_a, g'_a are suitable coupling constants parameterizing the strength of the interactions. Clearly, the Fierz rearranged charged current structures are included. We have neglected for simplicity a larger set of interactions.

In Eq. (1), the factor with the electron fields ψ_e is proportional to $1 - \vec{\sigma} \cdot \vec{v}$, where $\vec{\sigma}$ is the electron spin or angular momentum and $\vec{v}$ is the electron velocity. Assuming that neutrino velocities are isotropically distributed, the two opposite helicity states of the electron are split in energy by an amount proportional to the difference between the densities of neutrinos and antineutrinos (Stodolsky, 1975), of the order,

$$\Delta E \sim G_F\, \rho |\vec{\sigma} \cdot \vec{v}| \sim 0.6 \times 10^{-24} |\vec{\sigma} \cdot \vec{v}| eV. \tag{2}$$

Assuming the largest lepton asymmetry which favours, say, neutrinos, $\rho = (6\pi^2)^{-1} n^3$ is the cosmological density of neutrinos n being the Fermi level (in eV) of the gas, bounded by observational and theoretical cosmological arguments resulting $n \leq 1$ [(Langacker *et al.*, 1983; Stodolsky, 1975) and references in (Duda *et al.*, 2001)]. Here we have considered $n = 1$. Let us note that the cosmological flux, of the order of 10^{13} cm^{-2} sec^{-1} (Langacker *et al.*, 1983) is larger than the flux of solar neutrinos on Earth, of the order of 6×10^{10} cm^{-2} sec^{-1} (Bahcall, 1989).

To easily see that external electrons of L and R enantiomers of a chiral molecule may have opposite helicities, let us follow a simple schema as in (Pérez-Díaz *et al.*, 1991). We first consider an axial nuclear conformation along z-axis with periodicity a so that an electron can be described by $\Phi = \phi(\rho) e^{iK\chi} e^{ikz} = |K, p\rangle$, where ρ is the radial coordinate, χ is the angle around z, K is the quantum number of the angular momentum L_z, and $k = (2\pi/a)p$, with $p = 0, \pm 1, \pm 2 ...$, are the eigenvalues of the momentum P_z ($\hbar = 1$), the ground state being $|0, 0\rangle$. If a perturbative helicoidal potential of the form $V_L = V_0 \exp[i(2\pi z/a) - \chi] + c.c.$ is considered, the state $|0, 0\rangle$ connects with $|+1, -1\rangle$ and $|-1, +1\rangle$ states, so that the first-order perturbed electronic state is

$$\Phi_L = c_0 |0, 0\rangle + c_1 |+1, -1\rangle + c_2 |-1, +1\rangle\,, \tag{3}$$

with $|c_1|^2 = |c_2|^2 \equiv C$, i.e., the electron follows the helix travelling along the positive and negative z direction with momentum P_z and the corresponding angular momentum L_z, acquiring a helicity given by

$$\langle \Phi_L | L_z P_z | \Phi_L \rangle = -4C\pi/a, \tag{4}$$

with $\hbar = 1$. Analogously, for a right-handed helicoidal potential, $V_R = V_0 \exp[i(2\pi z/a) + \chi] + c.c.$, it can be seen that the first-order perturbed electronic state is then,

$$\Phi_R = c_0 |0, 0\rangle + c_1' |+1, +1\rangle + c_2' |-1, -1\rangle\,, \tag{5}$$

with $|c_1'|^2 = |c_2'|^2 = C$, which gives a positive helicity $\langle \Phi_R | L_z P_z | \Phi_R \rangle = 4C\pi/a$, ($\hbar = 1$), i.e.,

$$\langle \Phi_R | L_z P_z | \Phi_R \rangle = -\langle \Phi_L | L_z P_z | \Phi_L \rangle \,. \tag{6}$$

The spin of the electron can be taken into consideration in the spin-orbit interaction so that L_z must be replaced with $J_z = L_z + S_z$. In a realistic chiral molecule and in the case that some electrons feel a chiral potential, the electronic states are not in general eigenstates of the helicity, but the mean value of the helicity has opposite sign for L and R enantiomers. The parameter $C < 1/2$ accounts for the degree of chirality. Thus we can conclude that interactions of these electrons with neutrinos would lead to an energetic difference between the two enantiomers of a chiral molecule. Since the neutrino flux is isotropic, its interaction with the electrons of a chiral molecule is the same irrespective of the orientation of the molecule. We note that the translational velocity of the molecule carrier (interstellar grains, meteorites, the Earth...) does not contribute to the helicity of the electrons. Inserting the absolute value of the adimensional helicity, $4C\pi\hbar/(am_e c)$, in $|\vec{\sigma} \cdot \vec{v}|$ of Eq. (2), with $C \approx 1/2$ for strong enough chirality, and a of the order of some Angstroms, Eq. (2) give us, for the case of a single electron without any enhancement mechanism, an estimation for the energetic difference between the two enantiomers. It results to be of the order of $\Delta E \sim 10^{-26}$ eV. This energy is smaller than the estimated energy difference due to internal electroweak electron-nucleus interaction through neutral currents Z^0.

It is known that electroweak electron-nucleus interaction in atoms is amplified by a factor Z^3, Z being the atomic number (Bouchiat an Bouchiat, 1974). Usually, in molecules, the energy splitting due to electroweak electron-nucleus interaction is estimated as the second-order perturbative energy together with the spin-orbit interaction H_{SO} which is proportional to $\alpha^2 Z^2$, Z being the atomic number of the heaviest nucleus and α the fine structure constant. In this simple model, the molecular functions give a non-zero first order perturbation term and it is not necessary to invoke a second order perturbation term in the same way as is considered in electron-nucleus interaction. Let us note that the total number of electrons with helicity must be considered. Although each chiral molecule has its own peculiarities, we can say that electrons described by linear combinations of three or more atomic orbitals of different atoms would present helicity. Assuming one of this electrons per atom, the total number of such electrons would be significant in a heavy molecule and the energy difference between the two enantiomers would result amplified by this number.

Although in this paper we have considered only relativistic (R) neutrinos, let us note that neutrinos may be non-relativistic (NR). Actually is well known that neutrinos are massive particles, so they propagate at a velocity lower than c. Cosmological neutrinos were produced close to c (few seconds after the Big Bang) but, since at least some of the neutrino masses are expected to be bigger than the temperature of the neutrino bath, most part of cosmological neutrinos became NR long time ago before the prebiotic era. Neutrinos may be Dirac (D) or Majorana (M) particles. Majorana neutrino is a special type of massive neutrino that, in contrast to the Dirac one (previously considered in this paper), is its own antiparticle. Slow enough neutrinos eventually fall into gravitational potential wells and become bound, leading to clustering (C) neutrinos. Most cosmological neutrinos however are non-clustering (NC) because they are too light. There is a particular situation, $NC - NR -$ Majorana neutrinos, in which the energy splitting between the two helicity states of the electron is $\Delta E^M_{NC-NR} \leq (14/\sqrt{\xi_i})\Delta E^D_R$, where ΔE^D_R is the energy splitting previously estimated, and ξ_i is a parameter related to the chemical potential and temperature of type $i = \mu, \tau$ neutrinos, satisfying $|\xi_{\mu,\tau}| \leq 6.9$ (Duda *et al.*, 2001). In consequence, following that model, the energy splitting due to neutrino interaction would be amplified. We must remark that, in order to retain net helicity of NR-Majorana neutrinos, it is necesary they were not gravitationally bound (NC) and they were slowed down without any interactions.

As a result of these amplifications, the estimated energy difference might approach the usual energy difference due to electroweak electron-nucleus interaction, which was calculated for certain nucleus of D-ribose obtaining 10^{-21} eV (Letokhov, 1975) and for the compound A-nor-2-thiacholestane resulting also 10^{-21} eV (Rein *et al.*, 1980). Finally we note that both electron-nucleus and electron-neutrino electroweak P-odd interactions would be always present in the type of chiral molecules here considered. In a macroscopic sample of a single enantiomer, L for example, each type of effect is multiplied by the number of molecules, leading to an appreciable energy difference between L and R macroscopic samples for each effect. However, it seems difficult to distinguish experimentally between the two effects unless the chiral sample is isolated from neutrinos. By contrast, in atoms and non chiral molecules, only the internal electron-nucleus electroweak interaction is present since the helicity of the electrons is zero.

Concerning the biological chiroselection, all proposed mechanisms of discrimination between the two enantiomers, even those producing very small effects, are usually taken in account since several amplification processes may be present along many years. This analysis explores a P-odd process not yet estimated in the context of enantiomeric discrimination, contributing to research completeness of all possible universal mechanisms involved in molecular chiroselection.

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The Role of Supernova Neutrinos on Molecular Homochirality

Pedro Bargueño · Ricardo Pérez de Tudela

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Abstract Electroweak parity violating interaction between supernova (SN) neutrinos and electrons of a simple chiral molecule is studied related to the origin of molecular homochirality. Appearance of supernova remnants inside molecular clouds favours the interaction of SN-neutrinos with interstellar molecules, leading to a energetic difference between the two enantiomers of the order of 10^{-5} eV. This energetic difference is closer to the thermic energy of the interstellar medium, so molecular homochirality could be enhanced in molecular clouds containing supernova remnants inside it due to neutrino interaction.

Keywords chiroselection · chiral molecules · neutrino-electron scattering · supernova neutrinos

Introduction

The origin of molecular homochirality is still an open and very interesting problem related to fundamental aspects of physics, chemistry, biology, etc (Cline 1996). The discovery of an excess of L-amino acids in the Murchison meteorite (Cronin and Pizzarello 1997) and the observation of infrared circular polarization from the Orion OMC-1 star-formation region (Bailey et al. 1998) have reinforced the idea of an extraterrestrial origin of biological homochirality. If we do find homochirality elsewhere in the universe, it will almost indicate either life or advanced prebiotic chemistry, so the importance of a detailed study of cosmic sources of homochirality is justified.

Parity violating effects and asymmetric photolysis can be included in the reduced group of cosmic precursors of chiral discrimination. It is accepted that the calculated

P. Bargueño (✉) · R. Pérez de Tudela
Instituto de Matemáticas y Física Fundamental,
Consejo Superior de Investigaciones Científicas, Serrano 123, 28006-Madrid, Spain
e-mail: pbdr@imaff.cfmac.csic.es

parity violating energy differences due to electroweak electrons-nuclei interaction mediated by Z^0 are $10^{-17} - 10^{-14}\,k\mathrm{T}$ at room temperature (see for example Laerdahl and Schwerdtfeger 1996), giving an enantiomeric excess of $10^{-17} - 10^{-14}$. In this case, some sort of amplification mechanisms are needed to take account for the observed homochirality in typical biomolecules.

Chiral molecules such as amino acids are known to interact differently with both polarizations of a circularly polarized light (CPL). Enantioselective photodestruction have been already observed in the laboratory using UV CPL as a light source (Nuevo et al. 2005). It has been suggested that the required CPL could be find in the Orion OMC-1 star-formation region, although appropriate mechanisms involving polarized light in the necessary wavelength range are still speculative. Other sources of CPL are: neutron stars, magnetic white dwarfs, reflection nebulae, etc (see, for example Bailey 2001). Concerning parity violating effects, it has been considered in a recent paper (Bargueño and Gonzalo 2006) the effect of cosmological neutrinos on this discrimination. Within this order of ideas, a speculation is made in a very interesting paper about a possible enantiomeric discrimination produced by SN-neutrinos (Cline 2005). In this new paper we have estimated this later SN-neutrino contribution on molecular homochirality (originally derived in a different way in Tsarev 1999). We begin reviewing neutrino–chiral-molecules P-odd interaction following a simple model and the main supernova reactions producing neutrinos, and finally we will estimate the energetic difference between two enantiomers of a chiral molecule due to collisions with SN-neutrinos.

The interaction between neutrinos and electrons via a weak P-odd process mediated by charged currents $W^{\pm}$ produces a split in energy of the two helicity states of an electron in the neutrino bath, the energy split being proportional to the difference between the densities of neutrinos and antineutrinos (Duda et al. 2001). This process could discriminate between the two enantiomers of a chiral molecule if their respective electrons have opposite helicity. A simple model explaining it has been considered in a previous article (Pérez et al. 1991). In that paper, the authors considered a single electron molecule with an axial nuclear conformation as well as a perturbative helicoidal potential. If a left-handed helicoidal potential is considered, the electron follows the helix travelling along the positive and negative axial direction with momentum P_z and angular momentum L_z, acquiring a helicity given by:

$$\langle \Phi_L | L_z P_z | \Phi_L \rangle = -\frac{4C\pi\hbar}{am_e c} \tag{1}$$

where $|\Phi_L\rangle$ is the electronic state corresponding to the L-enantiomer, a is the potential periodicity and $C < 1/2$ accounts for the degree of chirality.

Analogously, for a right-handed helicoidal potential we have:

$$\langle \Phi_R | L_z P_z | \Phi_R \rangle = -\langle \Phi_L | L_z P_z | \Phi_L \rangle. \tag{2}$$

Following this simple scheme it can be seen that the electrons of the two enantiomers have opposite helicities.

The energy splitting of the electron states of a chiral molecule due to interactions with neutrinos has been recently studied (Bargueño and Gonzalo 2006). The interaction, mediated by weak charged currents, is based on the Hamiltonian,

$$H(V,A) = \frac{G_F}{\sqrt{2}} \Sigma_{a=V,A} (\overline{\psi}_\nu \Gamma_a \psi_\nu)[\overline{\psi}_e \Gamma^a (g_a + g'_a \gamma_5)\psi_e] + H.c. \tag{3}$$

where all the fields, constants and matrices have been defined elsewhere (Halzen and Martin 1984). The factor with the electron fields ψ_e is proportional to $1 - \vec{\sigma} \cdot \vec{v}$, where $\vec{\sigma}$ is the electron spin or angular momentum and $\vec{v}$ is the electron velocity. Assuming the largest neutrino asymmetry which favours, say, neutrinos, $\rho = (6\pi^2)^{-1} n^3$ is the number density of neutrinos n being the Fermi level (in eV) of the gas, the energy splitting is of the order

$$\Delta E \sim G_F \, \rho |\vec{\sigma} \cdot \vec{v}| \sim 0.6 \times 10^{-24} |\vec{\sigma} \cdot \vec{v}| = \frac{4C\pi\hbar}{am_e c} \rho G_F \quad eV\,. \tag{4}$$

The main characteristic of this energy splitting is that it is proportional to the difference between the number density of neutrinos and antineutrinos. If there is the same amount of neutrinos and antineutrinos interacting with chiral molecules, this effect is null. The natural questions that arise now are: what are the main sources of cosmic neutrinos and, does it exist any neutrino-antineutrino asymmetry related to this sources?.

Cosmological neutrinos have been studied in this context in our previous paper, leading to a small energetic discrimination of the order of 10^{-26} eV in the case of a chiral molecule with a single electron. Now, we focus our attention on an important consequence of stellar evolution; stars that end their lives like supernova explosions ejecting a great amount of neutrinos and antineutrinos.

Supernova Neutrino–antineutrino Production

Supernova of type II occurs at the end of the stellar evolution of certain massive stars. After successive nuclear burning, the structure of the star consist in an iron core surrounded by an structure of burning layers of silicon, oxygen, neon, carbon, helium and hydrogen. The iron core is expected to collapse into a neutron star or a black hole releasing a big amount of energy, the most of it is expected to be converted into neutrinos. The main reactions producing neutrinos and antineutrinos in a SN II are:

$$e^- + (Z, A) \xrightarrow{W^\pm, Z^0} (Z, A) + e^- + \nu + \bar{\nu} \text{ (Bremsstrahlung)} \tag{5}$$

$$e^- + p \xrightarrow{W^\pm} n + \nu_e \tag{6}$$

$$e^- + (Z, A) \xrightarrow{W^\pm} \nu_e + (Z-1, A) \tag{7}$$

$$e^+ + e^- \xrightarrow{W^\pm, Z^0} \nu + \bar{\nu} \quad \text{(pair annihilation)} \tag{8}$$

$$\textit{plasma excitation} \xrightarrow{W^\pm, Z^0} \nu + \bar{\nu} \quad \text{(plasmon decay)} \tag{9}$$

$$e^- + \gamma \xrightarrow{W^\pm, Z^0} e^- + \nu + \bar{\nu} \quad \text{(photoannihilation)} \tag{10}$$

We are only interested in reactions producing asymmetries between the number of neutrinos and antineutrinos, so we focus our attention on Eqs. (6) and (7).

Estimation of the Energy Split and Consequences

To estimate the energy split due to SN-neutrino–electron interaction, we consider that the momentum distribution of neutrinos and antineutrinos follows the Fermi–Dirac distribution (with zero chemical potential). The number distribution is therefore

$$n_{\nu_i}(T_\nu) = \frac{1}{(2\pi)^3}\int d^3p\,\frac{1}{\exp(p/T_\nu)+1} = \frac{3\xi(3)}{4\pi^2}T_\nu^3, \qquad (11)$$

where $\xi(3) \approx 1.20205$ is Riemann's zeta function.

Recent studies on the spectrum of SN-neutrinos constrain the Fermi–Dirac temperature between 4.8 and 6.6 MeV for the case of zero chemical potential and ν_μ, $\bar{\nu}_\mu$ neutrinos (Yoshida et al. 2005). Introducing Eq. (1) for the helicity term in Eq. (4), and considering $T_\nu = 5$ MeV in Eq. (11) we get in Eq. (4) an energy splitting of the order of 10^{-1} kT assuming a room temperature of 10 K for the interstellar medium and a molecule with a single electron. This leads to an enantiomeric excess of 10^{-1}.

Let us note that the total number of electrons with helicity must be considered. Assuming one of this electrons per atom, the total number of such electrons would be significant in a heavy molecule, eventually reaching the ideal situation of total homochirality without invoking any kind of amplification mechanisms, in contrast with the usual Z^0-mediated electroweak interactions referred previously in the introduction.

Concerning the detectability of homochirality in space molecules, stellar evolutionary models predict massive stars will die in supernova explosions near where they were born. It follows that supernova remnants associated with the molecular clouds from which their progenitors were born must have arisen from massive star, core-collapse supernovas. Some attempts to measure extraterrestrial homochirality have been carried out in the past (MacDermott et al. 1996).

Although the effect of SN-neutrino emission is considerably important only in the surroundings of a SN remnant, we propose that it might be eventually included in very sensitive future experiments searching for homochirality.

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Could dark matter or neutrinos discriminate between the enantiomers of a chiral molecule?

P. Bargueño[1,2(a)], A. Dobado[3] and I. Gonzalo[4]

[1] *Instituto de Matemáticas y Física Fundamental (CSIC) - Serrano 123, 20006 Madrid, Spain, EU*
[2] *Departamento de Química Física, Universidad de Salamanca - 37008 Salamanca, Spain, EU*
[3] *Departamento de Física Teórica I, Universidad Complutense de Madrid - 28040 Madrid, Spain, EU*
[4] *Departamento de Óptica, Universidad Complutense de Madrid - 28040 Madrid, Spain, EU*

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Abstract – We examine the effect of cold dark matter on the discrimination between the two enantiomers of a chiral molecule. We estimate the energy difference between the two enantiomers due to the interaction between fermionic WIMPs (weak interacting massive particles) and molecular electrons on the basis that electrons have opposite helicities in opposite enantiomers. It is found that this energy difference is completely negligible. Dark matter could then be discarded as an inductor of chiroselection between enantiomers and then of biological homochirality. However, the effect of cosmological neutrinos, revisited with the currently accepted neutrino density, would reach, in the most favorable case, an upper bound of the same order of magnitude as the energy difference obtained from the well-known electroweak electron-nucleus interaction in some molecules.

Introduction. – The origin of biological homochirality, that is, the almost exclusive one-handedness of chiral molecules in biological organisms, is a fundamental problem for which there is not yet a convincing solution. Several mechanisms have been proposed to explain chiroselection among the two possible enantiomers of a chiral molecule (see, for example, [1–3] and references therein). These mechanisms involve chance, β-radiolysis [4], circularly polarized light [5–7], magnetic fields [8,9], and violation of parity in the weak interaction (see below).

The discovery of an excess of L-amino acids in meteorites [10,11] has reinforced the idea of an extraterrestrial origin of biological homochirality [1,12]. In this context, universal mechanisms of chiroselection such as parity violation in weak interactions would acquire special interest in spite of their tiny effects, without, of course, underestimating other mechanisms.

The effect of electroweak interactions between electrons and nuclei mediated by the Z^0 have been extensively studied and observed in atoms (see the review [13]), and only predicted in molecules, where an energy difference between the two enantiomers of chiral molecules has been estimated to be between 10^{-16} and 10^{-21} eV [14–18]. In the laboratory, no conclusive energy difference has been reported in experimental spectroscopic studies reaching an energy resolution of about 10^{-15} eV [19].

The above tiny energy difference would require a powerful mechanism of amplification in order to induce a real enantioselective effect. Otherwise the small energy difference would be masked by the natural broadening of the energy levels of the molecule, thermal fluctuations and environment interactions, which do not discriminate, in average, between L and D enantiomers. There is active research on amplification mechanisms in which a permanent although very small interaction acting always in the same enantioselective direction, and under appropriate conditions, could lead to an effective enantioselection. Some mechanisms are based on nonlinear autocatalytic processes of polymerization or crystallization along a large period of time [20,21]. Another one involves a second-order phase transition below a certain critical temperature [22] that could work at low temperatures such as those of the interstellar space. However, theoretical or experimental conclusive results from the diverse mechanisms to amplify enantioselection based on electroweak energy difference, are not yet at hand (*e.g.*, [23,24]).

(a) E-mail: pbdr@imaff.cfmac.csic.es

Another universal mechanism that could discriminate between the two enantiomers of a chiral molecule and that involves weak interaction is neutrino-electron axial-vector interaction mediated by charged electroweak bosons $W^{\pm}$. This process discriminates on the basis of an asymmetry between the number of neutrinos and antineutrinos, and on the fact that electrons of opposite (L,R) enantiomers have opposite helicity. Considering the cosmological relic sea of neutrinos, the estimated energy difference between the two enantiomers was found to be even lower than the value 10^{-21} eV mentioned above [25]. However, it could increase significantly under bigger neutrino fluxes, as in supernova remnants [26] assumed that big molecules could survive in the surroundings. Revisited assumptions about the number density of cosmological neutrinos in the relic sea lead to an increase of the mentioned energy difference, as we shall see in the next section.

Looking for other universal mechanisms acting also outside of the Earth, we analyze here the possible enantioselective effect of chiral dark matter on chiral molecules.

The existence of dark matter is inferred from astrophysical observations in light of studies of the dynamics of stars in the local disk environment, rotation curves for a large number of spiral galaxies, gravitational lensing by clusters of galaxies and some large-scale studies of the Universe (for a recent review of experimental searches for dark matter see, for example, [27]). A vast variety of candidates has been proposed for dark-matter content, from baryonic to non-baryonic matter. The non-baryonic candidates are basically postulated elementary particles beyond the standard model which have not been discovered yet, like axions, WIMPs (Weak Interacting Massive Particles) and other exotic candidates. The baryonic candidates are the Massive Compact Halo Objects (Macho) [28]. Another important difference is the hot *vs.* cold dark matter. A dark-matter candidate is called hot if it moves at relativistic speeds at the time when galaxies could just start to form, and cold if it moves non-relativistically at that time. The problem is that hot dark matter cannot reproduce correctly the observed structure of the Universe. Therefore, we focus our attention on cold dark matter. The fact that dark matter interacts weakly with matter makes its detection very difficult [27]. However, many experiments are currently in progress in order to reach this goal.

Here we estimate the energy difference between the two enantiomers of a chiral molecule, due to the weak-type interaction between non-baryonic cold dark matter (specifically WIMPs) and molecular electrons with non-zero helicity. Experimental results on dark matter are used. Given the resemblance in the procedure with the energy difference induced by cosmological neutrinos, estimated in a previous work [25], we first recall this procedure at the time we improve the result we obtained in that work.

Energy difference between opposite enantiomers induced by cosmological neutrinos. – Following a previous work [25], we consider neutrino-electron interactions mediated by the axial-vector Hamiltonian density,

$$H = \frac{G_{\mathrm{F}}}{\sqrt{2}} \bar{e}\gamma^{\mu}(g_V - g_A\gamma_5)e\bar{\nu}\gamma_{\mu}(1-\gamma_5)\nu, \qquad (1)$$

where G_{F} is Fermi's constant, $e(\nu)$ denotes the electron (neutrino) spinor field, $\bar{e}(\bar{\nu})$ is its adjoint spinor, γ^{μ} are the Dirac matrices (regarded as a four-vector), $\gamma^5 = i\gamma^0\gamma^1\gamma^2\gamma^3$, and $g_{V,A}$ are suitable coupling constants that parameterize the strength of the interactions. As was discussed for example in [29], in the non-relativistic limit it is possible to make the following approximations for the dominant temporal components of the four-vectors appearing in the above Hamiltonian:

$$\begin{aligned} \bar{e}\gamma^{\mu}\gamma_5 e &\sim \vec{\sigma}_e \cdot \vec{v}_e, \\ \bar{\nu}\gamma_{\mu}\nu &\sim n_{\nu} - n_{\bar{\nu}} \qquad \text{(Dirac neutrinos)}, \\ \bar{\nu}\gamma_{\mu}\gamma_5\nu &\sim n_{\nu_l} - n_{\nu_r} \qquad \text{(Majorana neutrinos)}, \end{aligned} \qquad (2)$$

where the number density differences, $n_{\nu} - n_{\bar{\nu}}$ and $n_{\nu_l} - n_{\nu_r}$ refer to neutrino-antineutrino and left-right helicity eigenstates, respectively. Obviously they are not zero only in the case where there is a net lepton number or helicity in the cosmic neutrinos background. We recall from [25] and [30] that for Dirac neutrinos the energy splitting obtained for the electron is

$$\Delta E \sim G_{\mathrm{F}} |(n_{\nu} - n_{\bar{\nu}})\langle \vec{\sigma}_e \cdot \vec{v}_e \rangle|, \qquad (3)$$

where the expected value of the electron helicity $\langle \vec{\sigma}_e \cdot \vec{v}_e \rangle$ takes opposite signs for the two opposite enantiomers, as we can see from a simplified chiral molecule model [31]. In this model, a dominant axial symmetry around axis Z, with a left(right)-handed perturbative potential of period a, is assumed, so that the electronic molecular states can be described by superposition of eigenstates of both angular momentum L_z and linear momentum P_z (eigenvalues $\hbar n(2\pi/a)$), *i.e.* $|M_L, n\rangle$, in the form

$$\Phi_L = c_0|0,0\rangle + c_1|+1,-1\rangle + c_2|-1,+1\rangle, \qquad (4)$$

$$\Phi_R = c_0|0,0\rangle + c_1|+1,+1\rangle + c_2|-1,-1\rangle \qquad (5)$$

with $|c_1|^2 = |c_2|^2 \equiv C$. These L and R states have then opposite helicities:

$$\langle \Phi_L | L_z P_z | \Phi_L \rangle = -4C\pi/a = -\langle \Phi_R | L_z P_z | \Phi_R \rangle. \qquad (6)$$

Notice that we are using all the time natural units where $\hbar = c = 1$. The spin of the electron can be taken into consideration by replacing L_z with $J_z = L_z + S_z$. In a realistic chiral molecule the electronic states would not be eigenstates of the helicity, but its mean value would have opposite sign for L and R enantiomers. The parameter $C < 1/2$ accounts for the degree of chirality.

We note that the velocity of the molecule carrier (interstellar grains, meteorites, the Earth...) does not contribute to the helicity of the electrons: If $\vec{P}_T$ is the translational momentum of the carrier, the electronic wave function $\Phi_{L(R)}$ must include the factor $e^{i\vec{P}_T\cdot\vec{R}}$ (here $\vec{R}$ is the position of the molecule), and the contribution of $\vec{P}_T$ to the electron helicity is then

$$\langle\Phi_{L(R)}e^{i\vec{P}_T\cdot\vec{R}}|\vec{L}\cdot\vec{P}_T|\Phi_{L(R)}e^{i\vec{P}_T\cdot\vec{R}}\rangle = \langle\Phi_{L(R)}|\vec{L}|\Phi_{L(R)}\rangle\cdot\vec{P}_T = 0\,, \tag{7}$$

since $\langle\Phi_L|\vec{L}|\Phi_L\rangle = \langle\Phi_R|\vec{L}|\Phi_R\rangle = 0$ as can be seen from eqs. (4), (5). We also remark that the particle flux is assumed to be isotropic, thus, its interaction with the electrons of a chiral molecule is the same irrespective of the orientation of the molecule.

The energy difference that we obtained, assuming complete neutrino-antineutrino asymmetry, with number density of about $10^{-2}\,\mathrm{cm}^{-3}$, $C=1/2$, $a\sim 1$ Ångström and the electron helicity given by eq. (6), was of the order of $10^{-26}\,\mathrm{eV}$ [25].

However, it has been recently suggested [29,32] that, in scenarios beyond the standard model, the neutrino-antineutrino density asymmetry $n_\nu - n_{\bar\nu}$ could be up to the order of ~ 10–$1050\,\mathrm{cm}^{-3}$. Although the extreme upper-bound density asymmetry seems to be excluded by considerations of primordial nucleosynthesis [33], we consider it to estimate an upper bound of the energy difference.

If we take the value $n_\nu - n_{\bar\nu}\sim 1000\,\mathrm{cm}^{-3}$, we then obtain an upper bound for the energy difference between enantiomers of the order of $10^{-21}\,\mathrm{eV}$, per molecular electron with non-zero helicity. Evidently this tiny energy needs massive amplification mechanisms as those mentioned at the beginning in order to induce an effective enantioselection.

Energy difference between opposite enantiomers induced by fermionic cold dark matter. – In a way similar to the neutrino-electron interaction considered above, we are now to estimate the electron energy splitting induced by the axial-vector interaction between a fermionic dark-matter candidate (typically a WIMP) and an electron. The relevant Hamiltonian density can be written as

$$H = \sum_i d_i\bar\chi\gamma_\mu(1-\gamma_5)\chi\bar\psi_i\gamma^\mu\gamma_5\psi_i, \tag{8}$$

where χ is the dark-matter spinor which can be a Dirac or a Majorana one. The index i runs through $i=e,u,d,s$, *i.e.*, we are considering also the interaction between the dark-matter particle and the u,d and s quarks. This will be important later in order to use the present experiments trying to measure the WIMP flux on Earth to set some bounds on the possible effect of dark matter on opposite enantiomers. Therefore, d_e, d_u, d_d and d_s are the coupling of the χ field to the different matter fields $e=\psi_e, u=\psi_u, d=\psi_d$ and $s=\psi_s$.

As WIMPs are typical examples of cold dark matter and heavy by definition, we can invoke again the non-relativistic limit. Thus, as it was the case of neutrinos, for Dirac WIMPs the term $\bar\chi\gamma_\mu\chi$ dominates with the temporal component of this vector being proportional to $n_\chi - n_{\bar\chi}$. For the Majorana case only the axial vector $\bar\chi\gamma_\mu\gamma_5\chi$ remains and its temporal component becomes proportional to $n_{\chi_l} - n_{\chi_r}$, as in eq. (2).

The expression for the corresponding electron energy splitting is similar to that of eq. (3),

$$\Delta E \sim d_e|\Delta n\langle\vec\sigma_e\cdot\vec v_e\rangle|, \tag{9}$$

where Δn is the appropriate number density difference corresponding to the Dirac or the Majorana case. In principle these differences depend on the unknown nature of the dark matter and its evolution along the Universe history. In the following we will write these differences as $|\Delta n| = \alpha n$, where n is the total WIMP number density. Clearly the parameter α is a measure of the degree of particle-antiparticle or left-right asymmetry present in the dark matter, respectively. For example, in the case of Dirac dark matter, $\alpha=1$ indicates that all WIMPs are particles with no antiparticles present and $\alpha=0$ means a complete particle-antiparticle symmetry. As in the neutrino case, interactions between molecular electrons with non-zero helicity and cold dark matter could lead to an energy difference between the two enantiomers of a chiral molecule whenever the parameter α is different from zero. To have an estimation of the energy difference, we consider the interaction between WIMPs and an electron of a chiral molecule. Let $\rho = nM_\chi$ be the energy density of those WIMPs, with M_χ being their mass and n their number density. The density of WIMPs trapped in the gravitational potential wall of the galaxy is expected to be of the order of $\rho\sim 0.3\,\mathrm{GeV\,cm}^{-3}$. Then the energy splitting can be written as

$$\Delta E \sim d_e\alpha\,\frac{\rho}{M_\chi}|\langle\vec\sigma_e\cdot\vec v_e\rangle|. \tag{10}$$

In order to see how important this splitting could be, we need to know which values of the coupling constant d_e are acceptable. In principle there is no any available experimental information about d_e. However, one reasonable assumption that could be done is that all the d_i couplings are at least of the same order of magnitude. In the absence of a theory of WIMPs this does not seem to be so bad an assumption since WIMPs does not interact strongly with matter. If this is the case, one can then use the present bounds on the elastic cross-section proton-χ to get some information about the size of the d_i couplings. In order to compute this cross-section, one needs to relate the quark-χ couplings with the proton-χ coupling. This can be done by using the effective Hamiltonian (see [34] and references therein)

$$H = -a_p 2\sqrt{2}\bar\chi\gamma_\mu\gamma_5\chi\bar p s^\mu p, \tag{11}$$

where p is the proton spinor and s^μ is its spin vector (here we are considering the Majorana case but the Dirac case can be treated in a similar way). The coupling a_p is defined as

$$a_p = \frac{1}{\sqrt{2}} \sum_{i=u,d,s} d_i \Delta q_i^{(p)} \,. \tag{12}$$

The constants $\Delta q_i^{(p)}$ (with $q_1 = u, q_2 = d$ and $q_3 = s$) are introduced through the proton matrix element

$$\langle p|\bar{\psi}_i \gamma^\mu \gamma_5 \psi_i|p\rangle = 2s^\mu \Delta q^{(p)}. \tag{13}$$

Experimentally we have $\Delta u^{(p)} \simeq 0.78$, $\Delta d^{(p)} \simeq -0.5$ and $\Delta s^{(p)} \simeq -0.16$. Then, by using standard methods, it is straightforward to compute the elastic proton-χ cross-section, which is given in the proton rest frame by

$$\frac{\mathrm{d}\sigma}{\mathrm{d}q^2} = \frac{\sigma_n}{4v_\chi \mu^2}, \tag{14}$$

where $\vec{q}$ is the momentum transfer, v_χ is the χ velocity, μ is the proton-χ reduced mass and

$$\sigma_n = \frac{12 a_p^2 m_p^2 M_\chi^2}{\pi (m_p + M_\chi)^2} \tag{15}$$

(m_p being the proton mass) is just the non-relativistic cross-section for vanishing momentum transfer. Nowadays there are many experiments around the world trying to detect WIMPs directly (visit the webpage in [35] for complete and upgraded report of their main results). Usually they set exclusion regions on the plane σ_n-M_χ. From the recent XENON10 2007 [35] we learn, for example, that, for $M_\chi \simeq 100\,\text{GeV}$, σ_n must be smaller than $10^{-43}\,\text{cm}^2$ and, for $M_\chi \simeq 1000\,\text{GeV}$, smaller than $10^{-42}\,\text{cm}^2$. Assuming for simplicity all the quark couplings to be the same, *i.e.* $d_q \simeq d_u \simeq d_d \simeq d_s$, we have $a_p \simeq 0.0072 d_q^2$. Then we get that for $M_\chi \simeq 100\,\text{GeV}$, $d_q^2 < 10^{-14}\,\text{GeV}^{-4}$ and for $M_\chi \simeq 1000\,\text{GeV}$, $d_q^2 < 10^{-13}\,\text{GeV}^{-4}$. As discussed above we now assume $d_e \sim d_q$. Then it is possible to set a bound on the energy splitting which turns to be very tiny even in best case corresponding to $M_\chi \simeq 100\,\text{GeV}$. We obtain in this case, with an electron velocity about 10^{-2}, $\Delta E \leqslant \alpha 10^{-44}\,\text{eV}$.

Conclusion. – We have analyzed the effect of cold dark matter on the discrimination between the two enantiomers of a chiral molecule whose external electrons have opposite helicities in the respective opposite enantiomers. The estimated energy difference between the two enantiomers, due to WIMP-electron interaction, is found to be extremely small, several orders of magnitude lower than that induced by the electron-nuclei weak interaction. Hence, dark matter would be discarded as inductor of chiroselection between enantiomers and then of biological homochirality. By contrast, the enantioselective effect of the cosmological relic sea of neutrinos acquires relevance with the current assumptions about the number density of cosmological neutrinos. In this case we obtain an energy difference between 10^{-23} and $10^{-21}\,\text{eV}$ for the two opposite enantiomers per molecular electron with non-zero helicity. The upper bound of the energy difference, although it could be excluded by reasons previously mentioned, reaches the same order of magnitude as the energy difference induced by the well-known electron-nucleus electroweak interaction in some molecules.

* * *

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Detection of parity violation in chiral molecules by external tuning of electroweak optical activity

Pedro Bargueño,[1,2,*] Isabel Gonzalo,[3,†] and Ricardo Pérez de Tudela[1,‡]
[1]*Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain*
[2]*Departamento de Química Física, Universidad de Salamanca, 37008 Salamanca, Spain*
[3]*Departamento de Óptica, Universidad Complutense de Madrid, 28040 Madrid, Spain*
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A proposal is made to measure the parity-violating energy difference between enantiomers of chiral molecules by modifying the dynamics of the two-state system using an external chiral field, in particular, circularly polarized light. The intrinsic molecular parity-violating energy could be compensated by this external chiral field, with the subsequent change in the optical activity. From the observation of changes in the time-averaged optical activity of a sample with initial chiral purity and minimized environment effects, the value of the intrinsic parity-violating energy could be extracted. A discussion is made on the feasibility of this measurement.

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I. INTRODUCTION

Since the prediction and subsequent discovery of parity violation in weak interactions [1,2], the role of discrete symmetries in fundamental interactions is an intriguing field of research. The effect of electroweak interactions between electrons and nuclei mediated by the Z^0 has been extensively studied and observed in atoms (see the review [3]) and only predicted in molecules, where an energy difference between the two enantiomers of chiral molecules has been estimated to be between 10^{-16} and 10^{-21} eV [4–8]. In the laboratory, no conclusive energy difference has been reported in experimental spectroscopic studies reaching an energy resolution of about 10^{-15} eV [9]. In addition, since the effect of parity violation in the optical activity (OA) was reported [10], several authors have focused their attention in the possibility of measuring the parity-violating energy difference (PVED) between enantiomers via optical rotation experiments, looking for time-dependent evolution of either chiral states [10–17] or parity states [18,19]. However, no experimental results have been reported up to date. The main difficulties for obtaining information about the PVED from OA experiments are the predicted very small size of the effect that can be masked by racemization processes and loss of phase coherence due to collisions with the environment.

In this work, we propose an alternative way of detecting the PVED in OA experiments. Section II gives an elementary description of the two-state system which describes chiral molecules, focusing on the role that plays the competition between parity-violating and tunneling effects in the OA. In Sec. III, we study the effect of introducing an external chiral field coupled to the dynamics of the chiral molecule on the OA, showing that it can be used to measure the PVED. Several cases are analyzed. In Sec. IV, we consider circularly polarized light (CPL) as the external chiral source and a general discussion is made. The conclusions are presented in Sec. V.

*pbdr@imaff.cfmac.csic.es
†igonzalo@fis.ucm.es
‡rpt@imaff.cfmac.csic.es

II. CHIRAL STATES, PARITY VIOLATION, AND OPTICAL ACTIVITY

It is well known that, in the absence of parity violation, the true stationary states of a chiral molecule are the eigenstates of parity. However, it has been shown that the effect of introducing a P-odd term in the Hamiltonian leads to a new set of energy eigenstates which, in certain situations, are the chiral states. For our purposes, it is enough to consider the electron-nucleon parity-violating potential as the mean contribution to this P-odd term. This can be included in a two-state model of a chiral molecule as a constant perturbation, H^{PV}, such that $H=H^0+H^{PV}$ is the total Hamiltonian of the system, with H^0 including only parity conserving terms. In such a situation, we can express the energy eigenstates, $|\pm\rangle$, as a linear combination of the chiral states, $|L,R\rangle$, as

$$\begin{pmatrix} |+\rangle \\ |-\rangle \end{pmatrix} = \begin{pmatrix} \cos\beta & \sin\beta \\ -\sin\beta & \cos\beta \end{pmatrix} \begin{pmatrix} |L\rangle \\ |R\rangle \end{pmatrix}, \tag{1}$$

where β is the mixing angle, obtained from the knowledge of the eigenvectors of this Hamiltonian H, getting

$$\tan 2\beta = \frac{2H_{LR}}{H_{RR}-H_{LL}} = \frac{\delta}{\epsilon_{PV}}, \tag{2}$$

where $\epsilon_{PV}\geq 0$ means $0\leq\beta\leq\pi/4$ implying that $|L\rangle$ is lower or equal in energy than $|R\rangle$. The energy splitting between the two eigenstates of H^0 is $2\delta>0$, where $\delta=\langle L|H^0|R\rangle$ is related to the height of the barrier of the double-well potential whose minima correspond to the respective L and R equilibrium conformations. The PVED is given by $|H_{RR}-H_{LL}| = |\epsilon_R-\epsilon_L| = |2\epsilon_{L,R}|$, with $\epsilon_L=\langle L|H^{PV}|L\rangle=-\epsilon_R=-\langle R|H^{PV}|R\rangle \equiv \epsilon_{PV}$. One can express the eigenvalues of the system as $E_\pm=E_0\mp\sqrt{\epsilon_{PV}^2+\delta^2}$, with $E_0=(H_{LL}+H_{RR})/2$. If $\epsilon_{PV}\to 0$, $\tan 2\beta\to\infty$ and we recover an equal-weighted superposition of chiral states. But if $|\epsilon_{PV}|\gg\delta$, $\tan 2\beta\to 0$ and the chiral states tend to be the energy eigenstates, providing a solution to Hund's paradox (the apparent stability of enantiomers despite not being in energy eigenstates) [20], as pointed out by Harris and Stodolsky [10].

In a general situation, if the state is $|L\rangle$ at $t=0$, the time evolution leads to the well-known oscillations between $|L\rangle$ and $|R\rangle$ states, the transition probability to the $|R\rangle$ state being

$$P_{|L\rangle\to|R\rangle}(t) = \frac{1}{2}\frac{\delta^2}{\delta^2+\epsilon_{PV}^2}\sin^2(t\sqrt{\delta^2+\epsilon_{PV}^2}), \tag{3}$$

which tends to zero if $|\epsilon_{PV}| \gg \delta$ ($|L\rangle$, in this case, tends to be an energy eigenstate). Note that $\hbar=1$.

As it is well known, the OA associated with the intrinsic chiral nature of some molecules leads to an opposite rotation of the plane of polarization of incident linear polarized light when it interacts with opposite enantiomers. It leads to an oscillating rotation angle of the polarization plane when the molecule is oscillating between two enantiomers. For a nonvanishing ϵ_{PV}, the OA is modified (electroweak OA), so that, for a molecule $|L\rangle$ at $t=0$ and $0\leq\beta\leq\pi/4$ ($\epsilon_{PV}\geq 0$), the rotation angle is given by

$$\Phi(t) = \Phi_L \frac{\epsilon_{PV}^2+\delta^2\cos(2t\sqrt{\epsilon_{PV}^2+\delta^2})}{\epsilon_{PV}^2+\delta^2}, \tag{4}$$

where Φ_L is the rotation angle when the molecule is in the $|L\rangle$ state. For $-\pi/4\leq\beta\leq 0$ ($\epsilon_{PV}\leq 0$), the rotation is given by

$$\Phi(t) = -\Phi_L \frac{\epsilon_{PV}^2+\delta^2\cos(2t\sqrt{\epsilon_{PV}^2+\delta^2})}{\epsilon_{PV}^2+\delta^2} = \Phi_R \frac{\epsilon_{PV}^2+\delta^2\cos(2t\sqrt{\epsilon_{PV}^2+\delta^2})}{\epsilon_{PV}^2+\delta^2}, \tag{5}$$

where $\Phi_R=-\Phi_L$ is the rotation angle when the molecule is in the $|R\rangle$ state.

In what follows, we will focus on the time average of the relative OA (ROA), which for $0\leq\beta\leq\pi/4$ is then given by

$$\left\langle \frac{\Phi(t)}{\Phi_L} \right\rangle_t = \frac{\epsilon_{PV}^2}{\epsilon_{PV}^2+\delta^2} \tag{6}$$

and for $-\pi/4\leq\beta\leq 0$ is given by

$$\left\langle \frac{\Phi(t)}{\Phi_L} \right\rangle_t = -\frac{\epsilon_{PV}^2}{\epsilon_{PV}^2+\delta^2}. \tag{7}$$

There are several cases:

(i) $|\epsilon_{PV}|\ll\delta$. In this situation, the averaged ROA tends to zero since the oscillations are almost symmetric between $|L\rangle$ and $|R\rangle$ as shown in Fig. 1 (solid line). Therefore, no information about the PVED can be extracted.

(ii) $|\epsilon_{PV}|\gg\delta$. In this case in which $|L\rangle$ and $|R\rangle$ tend to be eigenstates, as mentioned above, the time-averaged value of ROA is very close to unity (as in a $|L\rangle$ state) and the extremely tiny oscillations around this value seem impossible to be observed. Let us remark that for having a time-averaged ROA very close to unity, it is not necessary for ϵ_{PV} to be many orders of magnitude greater than δ. For instance, see the case $|\epsilon_{PV}|=5\delta$ plotted with dotted line in Fig. 1.

(iii) If $|\epsilon_{PV}|$ is comparable to δ, the competition between these magnitudes determines the behavior of the OA oscillations giving place to significative shifts in the time average of the ROA. This is illustrated in Fig. 1, where we include the particular case $|\epsilon_{PV}|=\delta$ (dashed line) in which the OA oscillations go from Φ_L to zero, that is, $\langle\Phi(t)/\Phi_L\rangle_t=1/2$. This situation in which $|\epsilon_{PV}|$ is comparable to δ is then the most favorable to measure PVED by OA experiments, as was already noted by Harris and Stodolsky [10].

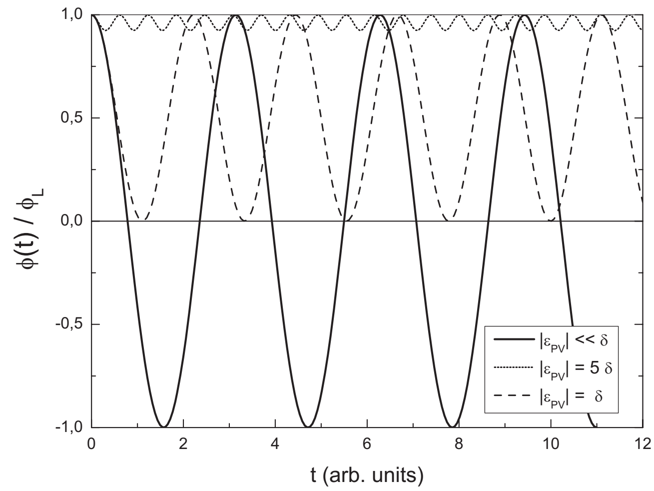

FIG. 1. Free oscillations of the relative optical activity assuming a $|L\rangle$ initial state for several cases $|\epsilon_{PV}|\ll\delta$ (solid line), $|\epsilon_{PV}|=5\delta$ (dotted line), and $|\epsilon_{PV}|=\delta$ (dashed line).

It is interesting to make some brief comments about the behavior of the time-averaged ROA under ϵ_{PV} due to Z^0 exchange in each one of the situations previously considered ($|\epsilon_{PV}|\ll\delta$, $|\epsilon_{PV}|\sim\delta$, and $|\epsilon_{PV}|\gg\delta$). It can be observed that the time-averaged ROA due to Z^0 exchange tends to unity as long as ϵ_{PV} increases, thus showing the expected behavior since when parity violation dominates the dynamics, no oscillations of the OA are expected. The main difference between the three considered situations is then that the approach to unity is faster as long as the value of ϵ_{PV}/δ is bigger.

Up to date, there have been several proposals to measure the electroweak OA. Harris and Stodolsky [10] proposed to prepare one of the chiral states and to measure the oscillations of the OA around a nonzero value. Quack [18,19] considered to measure oscillations of OA from an initially prepared $|+\rangle$ or $|-\rangle$ state. Harris [16] and MacDermott and Hegstrom [17] pointed out the difficulties of these proposals, suggesting to apply an external electric field to enhance the OA. The most recent work in this line [17] focuses on the measurement of PVED by means of separating the states $|+\rangle$ and $|-\rangle$ using an inhomogeneous electric field. The authors calculate the OA of the separated states, which is given by $\Phi_\pm\sim\pm\Phi_L(\epsilon_{PV}/\delta)$, and show that it should be measurable within the capabilities of state-of-the-art polarimeters.

In the next section, we describe an alternative method that would allow us to measure the PVED by means of an external chiral field (in particular CPL). We will see that the internal dynamics driven by parity violation and tunneling can be controlled with this field.

III. EXTERNAL CONTROL OF OPTICAL ACTIVITY AND CONSEQUENCES FOR THE DETECTION OF THE PVED

Our proposal lies in the apparent trivial fact that the intrinsic molecular PVED could be compensated by an external chiral perturbation. In this case, the electroweak OA would change accordingly. We consider now that the zeroth-order Hamiltonian includes both H^0 and H^{PV}. If a chiral perturbation, H', satisfying $\epsilon' = \langle L|H'|L\rangle = -\langle R|H'|R\rangle$, is applied, the new mixing angle β' is obtained by an analogous method to that followed to get Eq. (2), so it is given by

$$\tan 2\beta' = \frac{\delta}{\epsilon_{PV} + \epsilon'}, \tag{8}$$

and Eq. (4) is then trivially modified as

$$\Phi(t) = \Phi_L \frac{\epsilon^2 + \delta^2 \cos(2t\sqrt{\epsilon^2 + \delta^2})}{\epsilon^2 + \delta^2}, \tag{9}$$

where $\epsilon \equiv \epsilon_{PV} + \epsilon'$. The time-averaged ROA expressions are then modified as

$$\left\langle \frac{\Phi(t)}{\Phi_L} \right\rangle_t = \frac{\epsilon^2}{\epsilon^2 + \delta^2}, \tag{10}$$

for $0 \leq \beta' \leq \pi/4$, and

$$\left\langle \frac{\Phi(t)}{\Phi_L} \right\rangle_t = -\frac{\epsilon^2}{\epsilon^2 + \delta^2}, \tag{11}$$

for $-\pi/4 \leq \beta' \leq 0$.

Let us consider the free time evolution of a molecule with $\epsilon_{PV} \neq 0$ in a well defined $|L\rangle$ state at $t=0$. In absence of the external chiral field, its time-averaged ROA is given by $\epsilon_{PV}^2/(\epsilon_{PV}^2 + \delta^2)$ as shown in Eq. (6). By applying now a chiral field of appropriate handedness and intensity, the time-averaged ROA given by Eq. (10) becomes zero when $\epsilon' = -\epsilon_{PV}$ (that is, $\epsilon = 0$), which permits to get a value of ϵ_{PV} if the external perturbation ϵ' is known. If the intensity of the external field is further increased, the averaged ROA reverses its sign being described by Eq. (11). An additional increase of the external field up to $\epsilon' = -2\epsilon_{PV}$ leads to a time-averaged ROA given by $-\epsilon_{PV}^2/(\epsilon_{PV}^2 + \delta^2)$, which is opposite to the initial one without any external chiral field. This behavior is shown in Fig. 2 for several cases. Let us now analyze how significant the changes are in the OA when ϵ' is of the order of ϵ_{PV} in the three cases mentioned in the preceding section.

(i) For $|\epsilon_{PV}| \ll \delta$, the dynamics is determined by tunneling but not by PVED. Since ϵ' is as small as PVED, there is no significant change in the OA of the molecule, as in the situation depicted in Fig. 1 with solid line.

(ii) For $|\epsilon_{PV}| \gg \delta$ (dotted line in Fig. 1), δ is so small in this case that although ϵ_{PV} could be compensated with ϵ', no changes in the time-averaged ROA would be observed in general due to very long tunneling time (too large for laboratory times or for keeping coherence). Among all the molecules reported in the review made by Quack [21], the most favorable molecule belonging to this case is D_2Te_2 whose calculated tunneling time of about 16 s is probably still too large for keeping molecular coherence as will be commented below.

(iii) Finally, in the most favorable case in which $|\epsilon_{PV}| \sim \delta$, we must distinguish three different situations:

(a) If $|\epsilon_{PV}| = \delta$, a measure of the time-averaged ROA (here is 1/2) would give already the value of ϵ_{PV} if δ is known. If δ is not known, the external chiral field can be applied in order to obtain zero or a change of sign in the averaged ROA, which permits a measure of ϵ_{PV} as explained above. Among the molecules reported by Quack [21], the only one satisfying this constraint is T_2S_2. However, its calculated tunneling time of about 16 s seems too large for keeping molecular coherence.

(b) If $|\epsilon_{PV}| < \delta$, these magnitudes must be related by a factor significantly lower than 10 to obtain an appreciable change in the averaged ROA when it goes to zero or when it reverses its sign (a factor of 10 gives an averaged ROA of about 10^{-2}, which is too close to zero for our purposes). Among the molecules reported by Quack [21], the calculated values of the molecule D_2Se_2 verify $|\epsilon_{PV}| = (2/3)\delta$, the tunneling time being of 55 ms. In this case, the averaged ROA is about 0.3 and a change to zero or to −0.3 by means of the external field could be appreciated. In the same review [21], the molecule H_2Te_2 is reported with tunneling time of 0.55 ms (more favorable for keeping coherence), however the calculated values verify $|\epsilon_{PV}| = \delta/10$ and the changes would be then difficult to be appreciable as was said.

(c) In the case $|\epsilon_{PV}| > \delta$, we note that if these magnitudes are related by a factor of about 10, the averaged ROA is already close to unity, which seems more favorable than other cases to detect a change to zero of the averaged ROA. To distinguish experimentally this last situation from that in which there is no ϵ_{PV} and the tunneling time is longer than laboratory times $[\Phi(t \to \infty) = \Phi_L]$, the external chiral field seems to be useful in the following way. Large tunneling times imply high-energy barriers, so an external chiral field that produces a small contribution ϵ' of the order of ϵ_{PV} could not induce an inversion of the molecule through the high barrier. However, if such a field is able to induce a zero averaged ROA, we can conclude that the external field is able to compensated the ϵ_{PV} value of an oscillating molecule. Among the molecules reported by Quack [21], there is no one in this case (c) with $|\epsilon_{PV}|$ and δ being comparable.

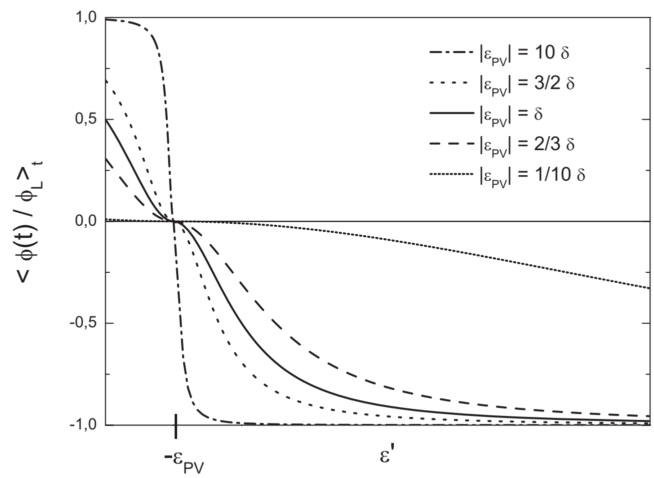

FIG. 2. Time average of the relative optical activity vs the perturbation energy (ϵ') supplied by the external chiral field for several cases. Note that there is a change of sign when $\epsilon' = -\epsilon_{PV}$ (see the text).

IV. CIRCULARLY POLARIZED LIGHT AS THE EXTERNAL CHIRAL FIELD AND GENERAL DISCUSSION

The conclusions extracted up to this point have been derived from the basic assumption that the applied external field is chiral. It is well known that a static uniform electric or magnetic field does not represent a truly chiral influence according to the generally accepted definition: true chirality is shown by systems existing in two distinct enantiomeric states that are interconverted by space inversion, but not by time reversal combined with any proper spatial rotation [22]. Nevertheless, if the electric or magnetic fields are nonuniform, true chirality may exist for certain configurations (see the extensive review by Ávalos and co-workers [23] about chiral influences and absolute asymmetric synthesis).

The true chirality of polarized photons can be easily demonstrated by considering the effects of parity and time reversal on the system in question. The photons in a beam of CPL radiation propagating as a plane wave are in spin angular-momentum states with a spin quantum number $s=1$ and quantum numbers $m_s=\pm 1$. A circularly polarized photon shows true chirality since parity interconverts the right and left circularly polarized forms, but time reversal does not. Then, our general statements about how to control the electroweak OA do apply using CPL as external chiral field.

The Hamiltonian, H', for the interaction of CPL with a molecule reads

$$H' = -\mu \cdot \mathbf{E}^{\pm}(t) - \mathbf{m} \cdot \mathbf{B}^{\pm}(t), \tag{12}$$

where μ and $\mathbf{m}$ are the electric and magnetic-dipole moment operators, $\mathbf{E}^{\pm}(t)$ and $\mathbf{B}^{\pm}(t)$ are the circularly polarized electric and magnetic fields, and the signs $\pm$ standing for the handedness of polarization. In the preceding section, the effect of H' on the enantiomers of a chiral molecules was denoted by $\epsilon' = \langle L|H'|L\rangle = -\langle R|H'|R\rangle$. The energy difference, $2\epsilon'$, between the two enantiomers due to the interaction with CPL was calculated by Shao and Hänggi [24]. The major contribution of this energy is given by

$$2\epsilon' = \pm \frac{16}{3} E B \omega \frac{R_{n0}}{\omega_{n0}^2 - \omega^2}, \tag{13}$$

where ω_{n0} is the resonance frequency nearest the incident frequency ω, $R_{n0} = \mathrm{Im}(\mu_{n0} \cdot \mathbf{m}_{n0})$ is the rotational strength, and a time average is made since the period of the electromagnetic radiation is much shorter than the molecular time oscillations.

In order to estimate the value of ϵ', we approximate the electric-dipole moment by ea_0 (a_0 is the Bohr radius) and the magnetic-dipole moment by the Bohr magneton ($e/2mc$) which leads to $R_{n0} \sim 10^{-18}$ Cm/Ts. If we consider $B=E/c$, $\omega^2/(\omega_{n0}^2 - \omega^2)$ of the order of unity [25], and $\omega \approx 3 \times 10^{15}$ rad s^{-1} (red light), we obtain

$$\epsilon' \sim \pm 3 \times 10^{-24} E^2 \text{ eV}. \tag{14}$$

This energy must be able to compensate the parity-violating energy ϵ_{PV} of the order between 10^{-16} and 10^{-18} eV (see Table II of Ref. [21].) for most of the chiral molecules. From the condition $\epsilon' = \epsilon_{PV}$, we obtain that the electric field of the CPL must be in the range

$$200 \leq E \leq 2000 \text{ V m}^{-1}, \tag{15}$$

which is easily achieved in the laboratory by usual lasers with powers in the range of from some mW cm^{-2} to about 1 W cm^{-2}.

Then, with this type of external field, it would be possible to control the time-averaged optical activity of the molecular sample provided each molecule keeps its coherence during its free time evolution.

Keeping coherence is one of the major experimental difficulties, as commented in several works (e.g., [17]). Since we try to measure the time average of the optical rotation, related to the time average of the oscillations, we do not require neither the initial time $t=0$ of their free oscillations be the same nor the ensemble of molecules oscillate together coherently. However, it is essential that each molecule preserves its individual coherence, evolving as Eq. (9). For this to occur, the time between collisions must be much longer than the molecular tunneling time. According to the discussion from [17], if we consider typical molecular beams (velocity of ~100 m/s and path length of about 1 m), we would require a tunneling time of $\tau < 10^{-2}$ s. Advances in molecular beams allow the molecules to be highly dilute at a few degrees Kelvin, with extremely low velocities, so still minimizing collisional effects. Moreover, it is possible to include helium droplets in molecular beams [26] which have the ability to capture molecules inside them [27]. This feature offers promising possibilities to improve the degree of isolation of the molecules. The superfluid nature of bosonic helium droplets below 2.17 K makes it possible for molecules placed inside them to evolve with zero friction, as in vacuum. In this scenario, the collision rate can be drastically reduced to almost zero and all the spurious thermal effects vanish due to the evaporation of helium. In such conditions, molecular coherence could be maintained for tunneling times much longer than 10^{-2} s.

Another aspect to be taken into account is that electromagnetic fields with very specific conditions could destroy tunneling, producing complete localization of the enantiomers [24,28]. Hence, the CPL applied to the molecular sample, as well as the linear polarized field whose optical rotation would be measured, must be far from these specific conditions.

Apart from these problems, the molecular sample must have initial chiral purity, e.g., L. In this sense, laser technology has prompted a considerable number of works dealing with the control of molecular handedness with the aim of obtaining chiral purity from racemic mixtures in molecular beams. Let us mention, for example, the proposal of Kucirka and Shekhtmann [29] using lasers with CPL in molecular beams, the works of Hoki *et al.* using linearly polarized femtosecond laser pulses in an oriented sample [30] or using three polarization components of electric fields in a randomly oriented sample in another laser scenario [31], and the work of Ma and Salam [32] using circularly polarized pulsed lasers.

V. CONCLUSIONS

A proposal is made to measure the parity-violating energy difference, $2\epsilon_{PV}$, between the enantiomers of a chiral molecule by measuring changes (induced by an external chiral field) in the time-averaged relative optical activity (ROA) of a molecular sample prepared with chiral purity at initial time. An external chiral field such as CPL generated in available lasers (lying in the range of mW cm^{-2}–W cm^{-2}) can induce an energy, ϵ', of the order of the parity-violating energy in chiral molecules, ϵ_{PV}. By varying the intensity of this field, the time-averaged ROA can be controlled so that when the external field compensates ϵ_{PV}, the time-averaged ROA becomes zero. The external field can also induce a change of sign in the time-averaged ROA. It would allow us to detect the parity-violating energy and even to measure it if ϵ' is known.

Several situations depending on the relative values of the parity-violating energy difference, $2\epsilon_{PV}$, and the splitting, 2δ, which determines tunneling times through the barrier, are discussed. The most favorable cases arise when these values are comparable (since the time-averaged ROA is then appreciable) and the tunneling time is short enough to preserve molecular coherence. One of the most promising candidates is D_2Se_2 [21], with theoretical values satisfying $|\epsilon_{PV}| = (2/3)\delta$ with tunneling time of 55 ms.

The observation of a time-averaged ROA does not require coherence in the ensemble of the molecules provided each molecule preserves its individual coherence in the oscillations at least during the experimental time. Advances in molecular beams open possibilities to minimize environment effects (and then decoherence) even by isolating chiral molecules inside helium clusters.

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Mikheev–Smirnov–Wolfenstein Effect in Chiral Molecules

PEDRO BARGUEÑO,[1,2] RICARDO PÉREZ DE TUDELA,[1] ISABEL GONZALO[3]

[1]*Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain*
[2]*Departamento de Química Física, Universidad de Salamanca, 37008 Salamanca, Spain*
[3]*Departamento de Óptica, Universidad Complutense de Madrid, 28040 Madrid, Spain*

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ABSTRACT: In a recent article (Phys Rev A 2009, 80, 012110), we have proposed an alternative method to measure the parity-violating energy difference between enantiomers of chiral molecules by modifying the dynamics of the two-state system using an external chiral field, in particular circularly polarized light. When this field is properly tuned, the two-state system becomes resonant, thus being maximal the probability of interconversion between enantiomers. In this work, we show that the resonance found in our previous work is identical to that found in two-flavor neutrino oscillations, known as Mikheev–Smirnov–Wolfenstein (MSW) resonance. We use some analogies between neutrinos and chiral molecules to derive some interesting properties of the oscillations between enantiomers. In particular, we obtain an expression for the transition probability between them when their energy difference is time-dependent. Int J Quantum Chem 00: 000–000, 2010

Key words: chirality; parity violation; oscillations

1. Introduction

As the prediction and subsequent discovery of parity (P) violation [1, 2] in weak interactions, the role of discrete symmetry breaking in fundamental physics is an intriguing field of research. Although weak interactions (between electrons and nuclei) mediated by the Z^0 boson have been extensively studied and observed in atoms [3], they have been only predicted in molecules. The importance of this symmetry-breaking could be intimately related to the origin of homochirality, that is, the almost exclusive one-handedness of the chiral molecules found in living systems (only L-amino acids and D-sugars). This is one of the most fascinating open problems, which links fundamental physics with the

Correspondence to: Isabel Gonzalo; e-mail: igonzalo@fis.ucm.es
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biochemistry of life [4]. In molecular systems, the theory of electroweak interactions predicts a parity-violating energy difference (PVED) between the two enantiomers of chiral molecules to be between 10^{-13} and 10^{-21} eV [5–10] but no conclusive energy difference has been reported, for example, in experimental spectroscopic studies of the CHBrClF molecule reaching an energy resolution of about 10^{-15} eV [11, 12].

Several proposals have been made by different authors to measure the PVED by optical methods, such as looking for the temporal oscillations of the optical rotation of a chiral sample where the two enantiomers L and R oscillate between them by coherent tunneling [13], taking also into account the damping due to the environment [14] and by amplifying the optical rotation by means of an electric field [15], or by measuring the optical rotation of superposition states that would have slightly different proportions of L (left) and R (right) conformations, using an inhomogeneous electric field in diluted molecular beams [16]. Other proposed mechanisms where the PVED could be manifested, deal with high-resolution spectroscopic measurements [17, 18] and sum frequency generation [19]. The main difficulties for obtaining information about the PVED from OA experiments is the predicted very small size of the effect that can be masked by racemization processes and loss of phase coherence due to collisions with the environment. In a previous work [20], we studied an alternative way of detecting the PVED in OA experiments by modifying the dynamics of the two-state system using an external chiral field, in particular, circularly polarized light. The intrinsic molecular parity-violating energy could be compensated by this external chiral field with the subsequent change in the optical activity. From the observation of changes in the time-averaged optical activity of a sample with initial chiral purity and minimized environment effects, the value of the intrinsic parity-violating energy could be extracted.

In this work, we show that the resonance found in our previous work is identical to that found in two-flavor neutrino oscillations, known as Mikheev–Smirnov–Wolfenstein (MSW) resonance [21–23], pointing out some analogies between neutrinos and chiral molecules under the two-state approach. This approach enables us to obtain, among other things, an expression for the transition probability between enantiomers when their energy difference is time-dependent.

2. Chiral States, Parity Violation and External Control of the Optical Activity

It is well known that in the absence of parity violation, the true stationary states of a chiral molecule are the eigenstates of parity. However, it has been shown that the effect of introducing a P-odd term in the Hamiltonian leads to a new set of energy eigenstates, which in certain situations, are the chiral states. For our purposes it is enough to consider the electron-nucleon parity violating potential as the leading contribution to this P-odd term. This can be included in a two-state model of a chiral molecule as a constant perturbation, H^{PV}, such that $H = H^0 + H^{\mathrm{PV}}$ is the total Hamiltonian of the system, with H^0 including only parity conserving terms. In such a situation, we can express the energy eingenstates, $|\pm\rangle$, as a linear combination of the chiral states, $|L, R\rangle$, as

$$\begin{pmatrix} |+\rangle \\ |-\rangle \end{pmatrix} = \begin{pmatrix} \cos\beta & \sin\beta \\ -\sin\beta & \cos\beta \end{pmatrix} \begin{pmatrix} |L\rangle \\ |R\rangle \end{pmatrix}, \tag{1}$$

where β is the mixing angle, obtained from the knowledge of the eigenvectors of this Hamiltonian H, getting

$$\tan 2\beta = \frac{2H_{LR}}{H_{\mathrm{RR}} - H_{\mathrm{LL}}} = \frac{\delta}{\epsilon_{\mathrm{PV}}}, \tag{2}$$

with $\epsilon_{PV} \geq 0$, which means $0 \leq \beta \leq \pi/4$ implying that $|L\rangle$ is lower or equal in energy than $|R\rangle$. The energy splitting between the two eigenstates of H^0 is 2δ, where $\delta = \langle L|H^0 + H^{\mathrm{PV}}|R\rangle = \langle L|H^0|R\rangle$ is related to the height of the barrier of the double well potential whose minima correspond to the respective L and R equilibrium conformations. The PVED is given by $|H_{\mathrm{RR}} - H_{\mathrm{LL}}| = |\epsilon_R - \epsilon_L| = |2\epsilon_{L,R}|$ with $\epsilon_L = \langle L|H^{\mathrm{PV}}|L\rangle = -\epsilon_R = -\langle R|H^{\mathrm{PV}}|R\rangle \equiv \epsilon_{PV}$. One can express the eigenvalues of the system as $E_\pm = E_0 \mp \sqrt{\epsilon_{\mathrm{PV}}^2 + \delta^2}$, with $E_0 = (H_{\mathrm{LL}} + H_{\mathrm{RR}})/2$. If $\epsilon_{\mathrm{PV}} \to 0$, $\tan 2\beta \to \infty$ and we recover an equal-weighted superposition of chiral states. But if $\epsilon_{\mathrm{PV}} >> \delta$, $\tan 2\beta \to 0$ and the chiral states tend to be the energy eigenstates, providing a solution to Hund's paradox (the apparent stability of enantiomers despite not being in energy eigenstates) [24], as pointed out by Harris and Stodolsky [13].

In a general situation, if the state is $|L\rangle$ at $t = 0$, the time evolution leads to the well known oscillations between $|L\rangle$ and $|R\rangle$ states, the transition probability to the $|R\rangle$ state being

$$P_{|L\rangle\to|R\rangle}(t) = \frac{1}{2}\frac{\delta^2}{\delta^2+\epsilon_{\rm PV}^2}\sin^2\left(\sqrt{\delta^2+\epsilon_{\rm PV}^2}t\right), \quad (3)$$

which tends to zero if $\epsilon_{\rm PV} >> \delta$ ($|L\rangle$, in this case, tends to be an energy eigenstate).

As it is well known, the OA associated with the intrinsic chiral nature of some molecules leads to an opposite rotation of the plane of polarization of incident linear polarized light when interacts with opposite enantiomers. It leads to an oscillating rotation angle of the polarization plane when the molecule is oscillating between the two enantiomers. For a nonvanishing ϵ_{PV}, the OA is modified (electroweak OA), so that for a molecule $|L\rangle$ at $t = 0$ and $0 \le \beta \le \pi/4$ ($\epsilon_{\rm PV} < 0$), the rotation angle is given by

$$\Phi(t) = \Phi_L \frac{\epsilon_{\rm PV}^2 + \delta^2\cos\left(2t\sqrt{\epsilon_{\rm PV}^2+\delta^2}\right)}{\epsilon_{\rm PV}^2+\delta^2}, \quad (4)$$

where Φ_L is the rotation angle, that is, the OA, when the molecule is in the $|L\rangle$ state. For $-\pi/4 \le \beta \le 0$ ($\epsilon_{\rm PV} < 0$), we have an equivalent expression for the the rotation angle. The time average of the relative OA (ROA), for $0 \le \beta \le \pi/4$, is then given by

$$\left\langle \frac{\Phi(t)}{\Phi_L} \right\rangle_t = \frac{\epsilon_{\rm PV}^2}{\epsilon_{\rm PV}^2+\delta^2} \quad (5)$$

From Eqs. (4) and (5) it is shown that the dynamics of the two-state system is governed by the PVED and tunneling effects. Thus, summarizing: if $\epsilon_{\rm PV} << \delta$, the average ROA tends to zero as the oscillations are almost symmetric between $|L\rangle$ and $|R\rangle$. If $\epsilon_{\rm PV} >> \delta$, $|L\rangle$ and $|R\rangle$ tend to be eigenstates, the time average value of ROA is very close to the unity, and the extremely tiny oscillations around this value seem impossible to be observed. If ϵ_{PV} is comparable to δ, the competition between these magnitudes determines the behavior of OA oscillations giving place to significative shifts in the time average of the ROA. This type of situation in which ϵ_{PV} is comparable to δ is then the most favorable to measure the PVED by OA experiments, as was already noted by Harris and Stodolsky [13].

The alternative method we describe in Ref. [20] to detect the PVED lies in the apparent trivial fact that the intrinsic molecular PVED could be compensated by an external chiral perturbation. In this case, the electroweak OA would change accordingly. In Ref. [20], we considered that the zeroth-order Hamiltonian included both H^0 and $H^{\rm PV}$. If a chiral perturbation, H', satisfying $\epsilon' = \langle L|H'|L\rangle = -\langle R|H'|R\rangle$, is applied, the new mixing angle β' is given by

$$\tan 2\beta' = \frac{\delta}{\epsilon_{\rm PV}+\epsilon'}, \quad (6)$$

and Eqs. (4) and (5) are then trivially modified as

$$\Phi(t) = \Phi_L \frac{\bar\epsilon^2 + \delta^2\cos\left(2t\sqrt{\bar\epsilon^2+\delta^2}\right)}{\bar\epsilon^2+\delta^2}, \quad (7)$$

and

$$\left\langle \frac{\Phi(t)}{\Phi_L} \right\rangle_t = \frac{\bar\epsilon^2}{\bar\epsilon^2+\delta^2}, \quad (8)$$

where $\bar\epsilon \equiv \epsilon_{\rm PV} + \epsilon'$.

If we consider the free time evolution of a molecule with $\epsilon_{\rm PV} \neq 0$ in a well defined $|L\rangle$ state at $t = 0$ in absence of an external chiral field, its time average ROA is given by $\epsilon_{\rm PV}^2/(\epsilon_{\rm PV}^2+\delta^2)$ as shown in Eq. (5). By applying now a chiral field and according to Eq. (8), the time-averaged ROA becomes zero when $\bar\epsilon = 0$, that is, $\epsilon' = -\epsilon_{\rm PV}$, which gives a value of $\epsilon_{\rm PV}$ if the external perturbation ϵ' is known. If the intensity of the external field increases, the average ROA changes its sign. Obviously, if we turn on the external field to the value $\epsilon' = -2\epsilon_{\rm PV}$, we arrive at an average ROA given by $-\epsilon_{\rm PV}^2/(\epsilon_{\rm PV}^2+\delta^2)$, which is the opposite value of the initial one without any external chiral field (for a complete discussion on the effect of circularly polarized light as the chiral perturbation in the OA in the three cases previously mentioned, see Ref. [20]).

We note that the key point is thus Eq. (6) as it describes the degree of mixing between chiral states, which is in essence the responsible of the appearance of the electroweak OA. From this equation, it is shown that when $\epsilon' = -\epsilon_{\rm PV}$, there is a resonance in the mixing angle, thus leading to a maximal probability of interconversion between chiral states shown in Eq. (3) substituting $\epsilon_{\rm PV}$ for $\bar\epsilon$ and taking $\bar\epsilon = 0$. In the following section, we point out some similarities between this effect and the corresponding one in neutrino physics.

3. Molecular MSW Effect

From the theoretical point of view, it is interesting to rewrite Eq. (6) as

$$\tan 2\beta' = \frac{\tan 2\beta}{1 - \frac{2\epsilon'}{\Delta E\cos 2\beta}}, \quad (9)$$

with $\Delta E = E_+ - E_- = 2\sqrt{\epsilon_{\rm PV}^2+\delta^2}$ and $\cos 2\beta = \frac{\epsilon_{\rm PV}}{\sqrt{\epsilon_{\rm PV}^2+\delta^2}}$.

Eq. (9) is formally equivalent to the very important expression which explains the MSW effect in neutrino physics [22, 23]. This effect consists in the change of the energy levels of the eigenstates of neutrinos when interact with electrons via charged-current scattering. This means that neutrinos in matter have a different effective mass than neutrinos in vacuum, and as neutrino oscillations depend upon the squared mass difference of the neutrinos, neutrino oscillations may be different in matter than they are in vacuum, as is shown in the following expression:

$$\tan 2\beta' = \frac{\tan 2\beta}{1 - \frac{2EV}{\Delta m^2 \cos 2\beta}}, \tag{10}$$

where β and β' are respectively the mixing angles in vacuum and matter, E is the neutrino energy, V is the charged-current potential, which leads to neutrino–matter interaction, and Δm^2 is the mass difference between neutrino mass eigenstates. There is an exact mapping between neutrino and chiral molecules oscillations as both situations can be described in terms of a two-level system (when we consider only oscillations between two neutrino flavors):

$$\begin{pmatrix} |R\rangle \\ |L\rangle \end{pmatrix} \leftrightarrow \begin{pmatrix} |\nu_e\rangle \\ |\nu_\mu\rangle \end{pmatrix}$$
$$\begin{pmatrix} |+\rangle \\ |-\rangle \end{pmatrix} \leftrightarrow \begin{pmatrix} |\nu_m^1\rangle \\ |\nu_m^2\rangle \end{pmatrix},$$

where the subscript m denotes neutrino states of well-defined mass.

When neutrinos go through the MSW resonance, $V = \Delta m^2 \cos 2\beta / 2E$, they have the maximal probability to change their nature, thus being in maximal mixing. Similarly, when the chiral perturbation is tuned to compensate the intrinsic parity violating effect, we recover the equal-weighted superposition of chiral states corresponding to $\bar{\epsilon} \to 0$.

Although the theoretical treatment needed to obtain Eqs. (2) and (6) is very simple (two-level system plus a constant perturbation), following the analogy with neutrino oscillations it is interesting to outline a different way of obtaining them from the time-dependent Schrödinger equation.

We can write the chiral states, $|L, R\rangle$ as a linear combination of the well-defined parity states, $|+,-\rangle$, by means of a unitary rotation matrix, U, so

$$|\psi_\alpha\rangle = \sum_k U^*_{\alpha k} |\psi_k\rangle, \tag{11}$$

where $\alpha = (L, R)$ and $k = (+,-)$. Let us suppose that we can write the Hamiltonian of the system as $H = H^0 + H'$, where H' is a chiral perturbation and H^{PV} is already included in H^0. If we define $\psi_{\alpha\beta} = \langle \psi_\beta | \psi_\alpha(t) \rangle$, it is easy to prove, from the time-dependent Schrödinger equation, that

$$i\frac{d}{dt}\psi_{\alpha\beta} = \sum_\eta \left(\sum_k U_{\beta k} E_k U^*_{\eta k} + \delta_{\beta\eta} E'_\beta \right) \psi_{\alpha\eta}(t), \tag{12}$$

with $H'|\psi_L\rangle = \epsilon'_L |\psi_L\rangle = \epsilon' |\psi_L\rangle$, $H'|\psi_R\rangle = -\epsilon'_R |\psi_R\rangle = -\epsilon' |\psi_R\rangle$, $H^0 |\psi_k\rangle = E_k |\psi_k\rangle$, and $\eta = (L, R)$. If we add and substract E_+ and we eliminate a common factor by means of the phase transformation

$$\psi_{\alpha\beta}(t) \to \psi_{\alpha\beta}(t) e^{-iE_+ t}, \tag{13}$$

we can write the relevant evolution equation for the chiral transition amplitudes as

$$i\frac{d}{dt}\psi_{\alpha\beta} = \sum_\eta \left(\sum_k U_{\beta k} \Delta E_{k+} U^*_{\eta k} + \delta_{\beta\eta} E'_\beta \right) \psi_{\alpha\eta}(t), \tag{14}$$

which can be written in matrix form as

$$i\frac{d}{dt}\Psi_\alpha = H_{\mathrm{eff}} \Psi_\alpha, \tag{15}$$

where

$$\Psi_\alpha = \begin{pmatrix} \psi_{\alpha\beta} \\ \psi_{\alpha\beta} \end{pmatrix}, \tag{16}$$

being $\alpha, \beta = |L\rangle$ or $|R\rangle$.

The evolution Eq. (15) has the structure of a Schrödinger equation with an effective Hamiltonian (in the chiral basis)

$$H_{\mathrm{eff}} = \frac{1}{2} \begin{pmatrix} -\cos 2\beta \Delta E + 2\epsilon' & \Delta E \sin 2\beta \\ \Delta E \sin 2\beta & \cos 2\beta \Delta E + 2\epsilon' \end{pmatrix}. \tag{17}$$

If we diagonalize this matrix by means of the orthogonal transformation

$$U'^T H_{\mathrm{eff}} U' = H^{\mathrm{diag}}_{\mathrm{eff}}, \tag{18}$$

then

$$H^{\mathrm{diag}}_{\mathrm{eff}} = \begin{pmatrix} -\sqrt{\delta^2 + \epsilon^2_{PV}} & 0 \\ 0 & \sqrt{\delta^2 + \epsilon^2_{PV}} \end{pmatrix}, \tag{19}$$

and the new unitary matrix is

$$U' = \begin{pmatrix} \cos\beta' & \sin\beta' \\ -\sin\beta' & \cos\beta' \end{pmatrix}. \tag{20}$$

From Eqs. (18), (19) and (20) one can prove that the new mixing angle satisfies Eq. (6). We point out that the energy splitting between parity states in presence of the chiral perturbation can be expressed as

$$\Delta E' = \sqrt{(\Delta E \cos 2\beta - 2\epsilon')^2 + (\Delta E \sin 2\beta)^2}. \quad (21)$$

If we write the effective Hamiltonian of Eq. (17) as

$$H_{\text{eff}} = \Delta E' \begin{pmatrix} -\cos 2\beta' & \sin 2\beta' \\ \sin 2\beta' & \cos 2\beta' \end{pmatrix}, \quad (22)$$

then, the evolution Eq. (15) can be rewritten as

$$i\frac{d}{dt}\Phi_\alpha = \frac{1}{2}\begin{pmatrix} -\Delta E'^2 & -2\,i\,\frac{d\beta'}{dt} \\ 2\,i\,\frac{d\beta'}{dt} & \Delta E'^2 \end{pmatrix}\Phi_\alpha, \quad (23)$$

with $\Phi_\alpha = U'\Psi_\alpha$. Letting $\frac{d\beta'}{dt} = 0$, the amplitudes of the chiral states are decoupled and we obtain the extension of Eq. (3) in case of having a non zero ϵ', that is,

$$P_{|L\rangle \to |R\rangle}(t) = \frac{1}{2}\frac{\delta^2}{\delta^2 + \bar{\epsilon}^2}\sin^2\left(\sqrt{\delta^2 + \bar{\epsilon}^2}\,t\right), \quad (24)$$

which has the same structure as the two-neutrino transition probability in vacuum.

If $\frac{d\beta'}{dt} \neq 0$ we have to take into account the term

$$\frac{d\beta'}{dt} = \frac{\sin 2\beta'}{\Delta E'}\frac{d\epsilon'}{dt}, \quad (25)$$

which includes a possible time-dependent effect present in the chiral Hamiltonian, H'. In this situation the chiral amplitudes are coupled and the solution of Eq. (23) depends on the explicit time dependence of ϵ'. To give an example in which Eq. (23) could be applied, we could consider, as previously done in Ref. [25], the electric and magnetic dipolar interactions of a chiral molecule with circularly polarized time-dependent fields. In this situation there is a time-dependent energy splitting betwen chiral states, which is a periodic function of time (see Eq. (6) in Ref. [25]), so our Eq. (23) does apply.

4. Conclusions

In this article, we have briefly summarized how to control the electroweak optical activity by means of external chiral fields, pointing out some formal relationships between chiral molecules and other physical system of great interest (mixing between two-flavor neutrinos). This analogy enable us to obtain an equation describing the time evolution of the transition probability between chiral states when the energy splitting between them is time-dependent.

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Parity violation and critical temperature of non-interacting chiral molecules

Pedro Bargueño [a,b,*], Isabel Gonzalo [c], Ricardo Pérez de Tudela [a], Salvador Miret-Artés [a]

[a] Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain
[b] Departamento de Química Física, Universidad de Salamanca, 37008 Salamanca, Spain
[c] Departamento de Óptica, Universidad Complutense de Madrid, 28040 Madrid, Spain

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ABSTRACT

Thermodynamical properties of non-interacting chiral molecules are studied under the two-state model in an asymmetric double well potential. The competition between thermal effects, the tunneling process and any pseudoscalar interaction (including electroweak parity violation) is governed by a critical temperature, T_c, where the heat capacity displays a maximum, and the entropy and the population difference between left and right conformations show an inflection point. This population difference becomes appreciable at temperatures below T_c, whereas, at higher temperatures, the racemization process is more and more important. The critical values of the entropy and heat capacity are constants and independent of the chiral system under study.

1. Introduction

Since the prediction and subsequent discovery of parity (P) violation [1,2] in weak interactions, the role of discrete symmetry-breaking in fundamental physics is an intriguing field of research. Although weak interactions (between electrons and nuclei) mediated by the Z^0 boson have been extensively studied and observed in atoms [3], they have been only predicted in molecules. The importance of this symmetry-breaking could be intimately related to the origin of homochirality, that is, the almost exclusive one-handedness of the chiral molecules found in living systems (only L-amino acids and D-sugars). This is one of the most fascinating open problems which links fundamental physics with the biochemistry of life [4]. In molecular systems, the theory of electroweak interactions predicts a parity violating energy difference (PVED) between the two enantiomers of chiral molecules to be between 10^{-13} and 10^{-21} eV [5–10] but no conclusive energy difference has been reported, for example, in experimental spectroscopic studies of the CHBrClF molecule reaching an energy resolution of about 10^{-15} eV [11,12].

Due to the fact that the parity violating signals are easily masked by thermal effects, it is highly desirable to reach cold or ultracold regimes in the laboratory [13–16]. The measurement of fundamental physical properties such as the PVED between enantiomers could be achieved by trapping molecules at temperatures in the milikelvin range or below and subsequently performing ultrahigh-resolution spectroscopic measurements of vibrational or electronic transitions.

In this work we study the effects of the PVED due to the electroweak interaction (or eventually another type of chiral influence), on the thermodynamical properties of a sample of non-interacting molecules composed by the two enantiomers of a chiral molecule, in thermal equilibrium. A canonical ensemble of chiral molecules is then considered. Each molecule is modeled by an asymmetric double well potential, the asymmetry being due to the PVED between enantiomers induced by a chiral perturbation (or pseudoscalar operator). A two-state model is used to describe the molecule. First, we analyze the different result obtained for the canonical average of a pseudoscalar operator in the case of a P-invariant Hamiltonian and a P-odd Hamiltonian. Then, we focus on some thermodynamic magnitudes and we obtain the canonical average of the energy, the Helmholtz free energy, the entropy and the specific heat.

A critical temperature, T_c, can be derived which separates the region where kT – and then thermal effects – tends to mask the PVED or (and) tunneling process, from a lower temperature region where the PVED or (and) tunneling become relevant over kT. In this low temperature region, both magnitudes, the PVED and tunneling between the two enantiomers L and R, would compete between them giving place to an enantiomeric excess in the equilibrium. From available chiral molecular data, it is shown that the range of T_c is from nanokelvin (when T_c is determined mainly by the PVED induced by electroweak interactions) to several Kelvin (when T_c is mainly determined by tunneling).

We point out the interest of measuring the anomalous behaviour of the specific heat of the sample in order to determine the electroweak PVED value.

* Corresponding author. Address: Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain.
E-mail addresses: pbdr@imaff.cfmac.csic.es (P. Bargueño), igonzalo@fis.ucm.es (I. Gonzalo), rpt@imaff.cfmac.csic.es (R.P. de Tudela), s.miret@imaff.cfmac.csic.es (S. Miret-Artés).

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2. The two-state model for a chiral molecule

In the absence of parity violation, the dynamics of a chiral molecule is well described by a symmetric double well potential. In this situation, the true stationary states of a chiral molecule are the (achiral) eigenstates of parity. The effect of including in the Hamiltonian the internal P-odd term given by the parity violating electron–nucleon electroweak interaction, H^{PV}, introduces an energy difference between the two minima of the double well potential, leading to a new set of energy eigenstates.

Let us consider the total Hamiltonian of the system $H = H^0 + H^{PV}$, with H^0 including only parity conserving terms. Using a two-state model, we choose the left and right chiral states basis, $|L\rangle$ and $|R\rangle$ (localized, respectively, in the left and right minima of the double well potential), in order to show clearly the parity properties of the Hamiltonian [17]:

$$H^0 + H^{PV} = \begin{pmatrix} E_0 & \delta \\ \delta & E_0 \end{pmatrix} + \begin{pmatrix} -\epsilon_{PV} & 0 \\ 0 & \epsilon_{PV} \end{pmatrix}, \qquad (1)$$

where H^{PV} is a pseudoscalar operator, i.e., $PH^{PV}P^{-1} = -H^{PV}$, P being the parity operator.

The eigenstates of H, here called $|\pm\rangle$, can be expressed as linear combinations of the chiral states, as

$$\begin{pmatrix} |+\rangle \\ |-\rangle \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} |L\rangle \\ |R\rangle \end{pmatrix} \equiv C \begin{pmatrix} |L\rangle \\ |R\rangle \end{pmatrix}, \qquad (2)$$

where the mixing angle, θ, obtained from the knowledge of the eigenvectors of H, is given by

$$\tan 2\theta = \frac{2H_{LR}}{H_{RR} - H_{LL}} = \frac{\delta}{\epsilon_{PV}}, \qquad (3)$$

where $\epsilon_{PV} \geqslant 0$ means $0 \leqslant \theta \leqslant \pi/4$ implying that $|L\rangle$ is lower or equal in energy than $|R\rangle$. The energy splitting between the two eigenstates of H^0 is $2\delta > 0$, where $\delta = \langle L|H^0|R\rangle$. This magnitude is related to the height of the barrier of the double well potential and it is inversely proportional to the tunneling time. The PVED is then given by $|H_{RR} - H_{LL}| = |2\epsilon_{PV}|$ with $\epsilon_{PV} = \langle R|H^{PV}|R\rangle = -\langle L|H^{PV}|L\rangle$. The eigenvalues of the system are given by

$$E_\pm = E_0 \mp \Delta \qquad (4)$$

with

$$E_0 = (H_{LL} + H_{RR})/2 \qquad (5)$$

and

$$\Delta \equiv \sqrt{\epsilon_{PV}^2 + \delta^2}. \qquad (6)$$

Now if $\epsilon_{PV} \to 0$, $\tan 2\theta \to \infty$ and we recover an equal-weighted superposition of chiral states. But if $|\epsilon_{PV}| \gg \delta$, $\tan 2\theta \to 0$ and the chiral states tend to be the energy eigenstates, providing a solution to Hund's paradox (the apparent stability of enantiomers despite not being in energy eigenstates [18], as pointed out by Harris and Stodolsky [17]). Thus, the internal dynamics of the two-state system can be understood in terms of the ratio between ϵ_{PV} and δ (see [19] and references therein).

3. Thermal properties of chiral molecules

3.1. General considerations

We can easily extend the Hamiltonian H to the case in which the P-odd part of H is any pseudoscalar (chiral) operator, due for example to the interaction with an external chiral field as one-handed circular polarized light. The generalized chiral operator, including all the chiral contributions, will be denoted by A and must be diagonal in the $|L\rangle$, $|R\rangle$ basis so that,

$$A = \begin{pmatrix} -a & 0 \\ 0 & a \end{pmatrix}, \qquad (7)$$

where $a = \langle R|A|R\rangle$ is the sum of all the eigenvalues, for the $|R\rangle$ state, of all the chiral operators considered. The eigenvalues of $H = H^0 + A$ are then $E_\pm = E_0 \mp \Delta$ where $\Delta \equiv \sqrt{a^2 + \delta^2}$.

Let us consider a canonical ensemble of non-interacting chiral molecules at temperature T described by the density matrix

$$\rho_\beta = Z^{-1} e^{-\beta H}, \qquad (8)$$

where $\beta = 1/(k_B T)$, H is the Hamiltonian of the molecule, Z is the partition function and $\mathrm{Tr}\rho_\beta = 1$. As is known, the thermal average of an observable X is given by

$$\langle X\rangle_\beta = \mathrm{Tr}(\rho_\beta X). \qquad (9)$$

Let us focus on the case that X is a pseudoscalar operator. If H is a P-even Hamiltonian, say H^0, it can be easily shown, following de Gennes [20], using the parity invariance of H^0 and the pseudoscalar character of X, that

$$\begin{aligned}\langle PXP^{-1}\rangle_\beta &= -\langle X\rangle_\beta = Z^{-1}\mathrm{Tr}\left(e^{-\beta H^0} PXP^{-1}\right) \\ &= Z^{-1}\mathrm{Tr}\left(P^{-1} e^{-\beta H^0} PX\right) = \langle X\rangle_\beta,\end{aligned} \qquad (10)$$

which implies $\langle X\rangle_\beta = 0$, that is, if the Hamiltonian is invariant under P, the expectation value of any pseudoscalar observable is zero in thermal equilibrium [20]. However, if the P-odd term A is added to the Hamiltonian, $H = H^0 + A$, we obtain, using the invariance of the trace of a product under cyclic reordering of it, that

$$\langle PXP^{-1}\rangle_\beta = Z^{-1}\mathrm{Tr}\left(e^{-\beta H^0} e^{-\beta A} PXP^{-1}\right) = Z^{-1}\mathrm{Tr}\left(e^{-\beta H_0} e^{\beta A} X\right)$$

or

$$|\langle X\rangle_\beta| = \left|Z^{-1}\mathrm{Tr}\left(e^{-\beta H_0} e^{\beta A} X\right)\right|, \qquad (11)$$

which means that, at thermal equilibrium, the measurement of any pseudoscalar observable gives a non-zero value.

In order to evaluate the expression (11) we choose the eigenstates $|\pm\rangle$ basis in which the partition function is easily expressed as

$$Z = e^{-\beta E_+} + e^{-\beta E_-}. \qquad (12)$$

The pseudoscalar operator X, with eigenvalues $\pm x$, and expression $X = x\sigma_z$ in the $|L,R\rangle$ basis (σ_z is a Pauli matrix), must be transformed to the $|\pm\rangle$ basis by means of the rotation matrix C defined in Eq. (2). The transformed operator $\tilde{X} = C^T X C$ so obtained is

$$\tilde{X} = x \begin{pmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & \cos 2\theta \end{pmatrix}. \qquad (13)$$

Finally, taking into account the expression $E_\pm = E_0 \mp \Delta$, a straightforward calculation gives

$$|\langle X\rangle_\beta| = |x \cos 2\theta| \tanh \beta\Delta, \qquad (14)$$

where $\cos 2\theta$ is due to be working in the basis of the eigenstates where X is non-diagonal, and $\tanh\beta\Delta$ comes from the thermal average. Notice that the derivation made here is general, with $\Delta = \sqrt{a^2 + \delta^2}$.

An example of operator X could be optical rotation, x being the rotation per molecule of the plane of polarization of non-resonant linear polarized light interacting with the chiral molecule. We note that since the effect of parity violation in the optical activity (electroweak optical activity) was reported [17], several authors have focused their attention on the possibility of measuring the PVED between enantiomers *via* optical rotation experiments looking for time evolution of chiral states [17,21], amplifying the optical rotation by means of an electric field [22], measuring the optical rotation of superposition of chiral states [23] and that of chiral states adding and external tuning of the electroweak optical activity [19]. Other proposed mechanisms where the PVED could be manifested deal with high-resolution spectroscopic measurements [24,25] and sum frequency generation [26]. Another example of operator X is, of course, the proper chiral part of the Hamiltonian, that is, the chiral operator A which becomes H^{PV} in the case of electroweak interactions.

Another magnitude of interest is the population difference between $|L\rangle$ and $|R\rangle$ states at a given T. Once the chiral states are expressed as linear combinations of the $|\pm\rangle$ states, we easily obtain,

$$n_L - n_R \equiv \langle L|\rho|L\rangle_\beta - \langle R|\rho|R\rangle_\beta = \cos 2\theta \tanh \beta\Delta, \tag{15}$$

where $\cos 2\theta = a/\sqrt{a^2+\delta^2}$ is the population difference at $T = 0$, which is the difference of probabilities for a single molecule of being in $|L\rangle$ and $|R\rangle$ states, as is easily seen from Eq. (2). The population difference could play the role of a long-range order parameter when interacting chiral molecules and possible phase transitions are to be considered.

From Eqs. (14) and (15) we note that the absolute value of the thermal average of X is, in fact, the absolute value of the product of its eigenvalue at zero temperature multiplied by the difference $n_L - n_R$.

3.2. Thermodynamic magnitudes and the critical temperature

Let us now consider the Hamiltonian with the parity violating electroweak contribution, i.e., $H = H^0 + H^{PV}$. The thermal average of the total energy in the $|\pm\rangle$ basis, is given by

$$\langle E\rangle_\beta = n_+E_+ + n_-E_- = E_0 - \Delta \tanh \beta\Delta, \tag{16}$$

where $n_\pm = \langle\pm|\rho|\pm\rangle_\beta$ and Δ is given by Eq. (6). Note that $\langle E\rangle_\beta$ tends to the lowest value of the energy, $E_0 - \Delta$, at zero temperature and to E_0 at high temperatures. This saturation value of the energy is due to the limited number of energy levels of the system which gives place to the so called Schottsky anomaly [27]. As we will be shown later on, this behaviour is responsible for the maximum in the heat capacity of the system.

The Helmholtz free energy, F, can be easily obtained as

$$F = -\frac{1}{\beta}\ln Z = -\beta^{-1}\ln(2e^{-\beta E_0}\cosh \beta\Delta) \tag{17}$$

and the entropy of the system, S, is given by

$$S = k_B(\ln Z + \beta\langle E\rangle_\beta) = k_B \ln(2e^{-\beta\Delta\tanh\beta\Delta}\cosh\beta\Delta), \tag{18}$$

where the argument of the logarithmic function is the number of accesible states. Let us note that its high and low temperature limits, $k_B\ln 2$ and zero, respectively, are properly recovered. Let us note that the free energy was derived previously in Ref. [28] in a different context. Finally, the heat capacity at constant volume is then expressed as

$$C_v = \frac{\partial\langle E\rangle_\beta}{\partial T} = T\frac{\partial S}{\partial T} = k_B\beta^2\Delta^2 \mathrm{sech}^2 \beta\Delta. \tag{19}$$

In Fig. 1, the difference $n_L - n_R$, the entropy and the heat capacity are plotted as a function of the temperature for two cases, zero (dashed curves) and non-zero (solid curves) ϵ_{PV} for the D_2Se_2 molecule with predicted values $\delta = \epsilon_{PV} = 10^{-14}$ eV [29]. The functional form of any of these three thermodynamic magnitudes shows the existence of a critical temperature T_c (vertical lines), where $n_L - n_R$ and entropy display an inflection point and the heat capacity a maximum. If the second derivative of, for example, the entropy, equals to zero, the corresponding critical temperature satisfies

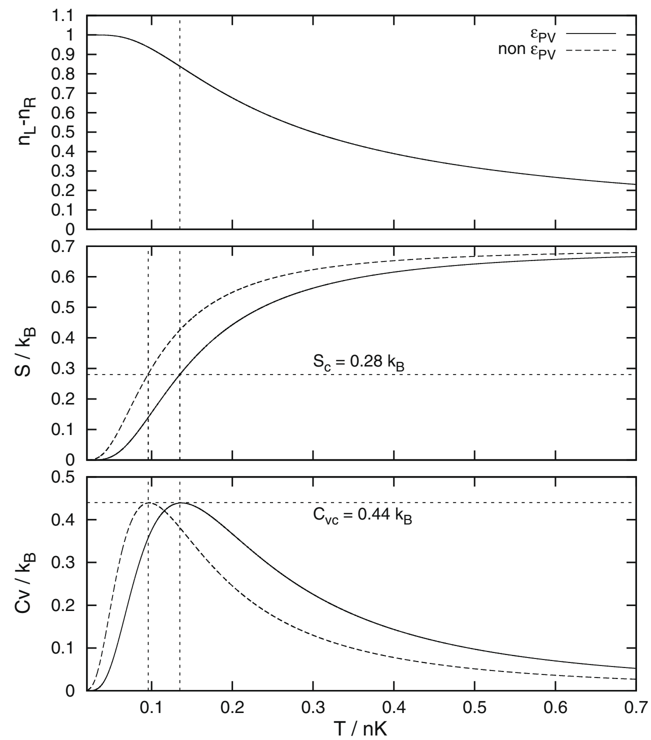

Fig. 1. Temperature dependence of $n_L - n_R$ (top panel), entropy (middle panel) and specific heat (bottom panel) functions for zero and non-zero ϵ_{PV} (with dashed and solid curves, respectively). Vertical and horizontal lines show, respectively, the critical temperature and the values of the depicted magnitudes at this temperature. We have taken $\epsilon_{PV} = \delta = 10^{-14}$ eV.

$$\beta_c\Delta \tanh \beta_c\Delta = 1, \tag{20}$$

where $\beta_c = 1/(k_BT_c)$. This critical condition reminds us the spontaneous magnetization condition from which the Curie temperature is defined [30]. Its solution can be expressed as

$$\beta_c\Delta \approx 1.2 \tag{21}$$

and, therefore, Eq. (21) can also be rewritten in a more transparent way as

$$T_c^2 \approx \frac{\delta^2}{(1.2\,k_B)^2} + \frac{\epsilon_{PV}^2}{(1.2\,k_B)^2} \equiv T_\delta^2 + T_{PV}^2, \tag{22}$$

where T_{PV} and T_δ are the temperatures associated with the presence of the diagonal elements of H^{PV} and non-diagonal elements of H^0 (tunneling) in the chiral states basis, respectively.

Taking E_0 as the origin of energies of our system, the values of the average energy, the Helmholtz free energy, the entropy and the specific heat at this critical temperature are easily expressed as

$$\begin{aligned}
&\langle E\rangle_{\beta_c} = \beta_c^{-1},\\
&F_c \approx 1.28\,\beta_c^{-1},\\
&S_c \approx 0.28\,k_B = k_B \ln \Omega_c,\\
&(C_v)_c \approx 0.44\,k_B.
\end{aligned} \tag{23}$$

Some of these values are plotted as horizontal lines in Fig. 1. It is interesting to note that, on one hand, $\langle E\rangle_{\beta_c}$ and F_c depend on the system under study, since the value of the critical temperature is given by Eq. (21) and Δ encodes information about the specific molecule. On the other hand, neither the entropy nor the specific heat depend on the system at this critical temperature. It is quite remarkable that both functions are constant for *any* chiral molecule where the two-state model applies.

At this point we must consider a more general case where there is also an extra pair of states. If this new pair is separated from the first one by a rotational energy, E_r, and $2\Delta \ll E_r$, the heat capacity will show a secondary maximum at higher temperatures, the first maximum remaining unaltered. Similarly, the entropy will display a second step. Therefore, the values of $(C_v)_c$ and S_c will remain the same. On the contrary, if $2\Delta \sim E_r$, we will have to extend our study to a system with more than two states.

At the critical point, the number of microscopic states which are compatible with the macroscopic description of the system is, from $S = k_B \ln \Omega$, $\Omega_c \approx [e^{1.2} + e^{-1.2}/e] = 1.32$, being far from the equiprobability condition.

Finally, we point out the possibility of measuring the heat capacity to obtain the critical temperature and, thus, to extract information about ϵ_{PV}.

3.3. Thermal effects versus tunneling and parity violation

In general, thermal effects tend to wash out the population difference $n_L - n_R$. It is interesting then to analyze the role of the temperature versus tunneling and parity violation in terms of the critical temperature. To this end, it is useful to rewrite Eq. (15) as

$$n_L - n_R = \left[1 + (\delta/\epsilon_{PV})^2\right]^{-1/2} \cdot \tanh\left[(\epsilon_{PV}/k_B T)\sqrt{1 + (\delta/\epsilon_{PV})^2}\right]. \quad (24)$$

At temperatures higher than T_c, the effect of ϵ_{PV} becomes masked by thermal effects according to the ratio $\epsilon_{PV}/(k_B T)$ shown in Eq. (24) and $n_L - n_R$ tends to zero.

At low temperatures, $T < T_c$, we have the following situations depending on the ratio δ/ϵ_{PV}, which is constant for a given molecule:

(i) $T_\delta \gg T_{PV}$ ($\delta \gg \epsilon_{PV}$). In this case, at $T < T_c \sim T_\delta$, the competition between tunneling and ϵ_{PV} according to the ratio δ/ϵ_{PV} affords a low population difference at low temperatures as shown in Eq. (24). In the limit case that $\epsilon_{PV} \to 0$, the double well becomes symmetric and $n_L - n_R$ becomes zero, the racemization occurring at any temperature. In this last situation, the effect of temperature only appears in the difference of populations of the equal-weighted (in L and R) superposition states $|\pm\rangle$, $n_+ - n_- = \tanh \beta\delta \geqslant 0$.

(ii) $T_\delta \ll T_{PV}$ ($\delta \ll \epsilon_{PV}$). Here, at $T < T_c \sim T_{PV}$, ϵ_{PV} dominates over δ but in spite of this, an appreciable value for $n_L - n_R$ is not expected due to the extremely long tunneling times which prevent reaching thermal equilibrium in laboratory times (except if the molecule could be synthesized at such an ultracold regime).

(iii) $T_\delta \sim T_{PV}$ ($\delta \sim \epsilon_{PV}$). In this interesting and important case, $n_L - n_R$ at $T < T_c$ is determined by the competition between tunneling and parity violation according to the ratio δ/ϵ_{PV} as shown in Eq. (24).

Table 1
ϵ_{PV}, δ and T_c are shown for some selected molecules. The orders of magnitude of ϵ_{PV} and δ have been taken from Table 2 of [29].

Molecule	ϵ_{PV} (eV)	δ (eV)	T_c (K)
H_2O_2	10^{-18}	10^{-4}	1
H_2S_2	10^{-16}	10^{-10}	10^{-6}
H_2Te_2	10^{-13}	10^{-12}	10^{-8}
D_2Se_2	10^{-14}	10^{-14}	10^{-10}
CHFBrCl	10^{-16}	Very small	10^{-12}

In Table 1, a short list of critical temperatures for some selected chiral molecules is presented. The order of magnitude of the predicted values of ϵ_{PV} and δ have been taken from Table 2 of [29], where these values are reported for an extensive list of chiral molecules. Let us note the different order of magnitude among critical temperatures corresponding to different molecules. In fact, these differences are associated with different ϵ_{PV}/δ ratios.

Finally, we remark that the critical value of the entropy, S_c, which separates the region of entropies in which $n_L - n_R$ is non-negligible, from the one governed by racemization, is independent of the molecule under study.

4. Conclusions

The thermodynamic study of an ensemble of non-interacting chiral molecules, carried out under the two-state model in an asymmetric double well potential, allows us to define a critical temperature, T_c, where the heat capacity displays a maximum, and the entropy and the population difference between left and right conformations, an inflection point. Below this T_c, the process due to parity violation dominates over the racemization induced by thermal effects. Moreover, the critical temperature can be expressed in terms of two internal temperatures T_{PV} and T_δ, each one associated with a given intrinsic process: parity violation and tunneling, respectively. It is quite remarkable that at the critical temperature, the entropy and the heat capacity at constant volume are independent on the chiral molecule; they are constant. We have pointed out the possibility of observing the critical temperature and then the PVED by measuring the heat capacity of the sample. We think that the critical temperature, which is a fingerprint of a given chiral molecule, should also be added in any handbook of chirality when the existence of ϵ_{PV} is confirmed.

We have shown that in a P-odd Hamiltonian the measurement of any pseudoscalar observable gives a non-zero value at thermal equilibrium. In particular, we mention that the optical activity could be one of such pseudoscalar observable. Work on the possibility to determine the PVED by optical activity measurements is now in progress.

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Towards the detection of parity symmetry breaking in chiral molecules

Isabel Gonzalo [a,*], Pedro Bargueño [b,c], Ricardo Pérez de Tudela [b], Salvador Miret-Artés [b]

[a] Departamento de Óptica, Universidad Complutense de Madrid, 28040 Madrid, Spain
[b] Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain
[c] Departamento de Química Física, Universidad de Salamanca, 37008 Salamanca, Spain

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ABSTRACT

We propose an optical rotation experiment to detect the electroweak parity-violating energy difference (PVED) between the two enantiomers of a chiral molecule. For some chiral molecules, it is shown theoretically that at low enough temperature, in the range from mK to few K, the competition between the PVED, tunneling between the two enantiomers and thermal effects leads to an enantiomeric excess in the thermodynamic equilibrium which is able to produce an optical rotation measurable by state-of-the-art ultrasensitive polarimeters. By means of mechanisms inhibiting tunneling, the sample would keep the enantiomeric excess at higher temperatures. Suitable chiral molecules are pointed out.

Since the effect of parity violation on the optical activity was reported by Harris and Stodolsky [1], several authors have focused their attention on the possibility of measuring the parity-violating energy difference (PVED) between the two enantiomers of a chiral molecule, *via* optical rotation or spectroscopic experiments.

Although parity violating electroweak interactions between electrons and nuclei have been extensively studied and observed in atoms [2], they have been only predicted in molecules. In chiral molecules, the electroweak interactions predict a PVED of the order from 10^{-13} to 10^{-21} eV depending on the molecule [3–9], but no experimental observation has been reported up to date even in very high-resolution spectroscopic experiments as those performed with the chiral molecule CHBrClF reaching an energy resolution around 10^{-15} eV [10,11].

The importance of the PVED could be linked, by means of appropriate amplifications, to the origin of biohomochirality, i.e., the exclusive presence of only one enantiomer in living systems (e.g., only L-amino acids and D-sugars), this being one of the most fascinating and fundamental open problems.

Several proposals have been made by different authors to measure the PVED by optical methods, such as looking for the temporal oscillations of the optical rotation of a chiral sample where the two enantiomers *L* (left) and *R* (right) oscillate between them by coherent tunneling [1], taking also into account the damping due to the environment [12] and by amplifying the optical rotation by means of an electric field [13], or by measuring the optical rotation of superposition states that would have slightly different proportions of *L* and *R* conformations, using an inhomogeneous electric field in diluted molecular beams [14]. Other proposed mechanisms where the PVED could be manifested, deal with high-resolution spectroscopic measurements [15,16] and sum frequency generation [17]. We proposed recently an optical rotation experiment to detect the PVED in a diluted molecular beam where the PVED, and then the optical rotation would change in sign or becomes null by means of an external circularly polarized light [18].

The difficulties to implement all these proposals in the laboratory are due to the extremely small value of the PVED that can be masked by loss of phase coherence due to the environment or thermal effects, which makes desirable to reach very small densities or/and very cold regimes during the measurements.

Here we discuss the possibilities of an optical rotation experiment to detect the PVED where neither the coherence of tunneling nor that of superposition states are necessary during the measurement. However, it is necessary to reach, during a stage of the experiment, a cold regime and, eventualy, a low enough density to obtain the enantiomeric excess required to be detected by an ultrasensitive polarimeter. This excess must be maintained at the polarimeter work conditions by means of mechanisms inhibiting tunneling as commented below.

Let us note that, although most of the current research in the cold and ultracold regimes focuses on atoms and diatomic molecules, recent work shows that it may be possible to cool large polyatomic molecules to ultralow temperatures as well (see [19], for example).

First let us recall that a chiral molecule is usually described by a symmetric double well potential where each minimum corresponds to each one of the chiral states, $|L\rangle$ (left) and $|R\rangle$ (right). If the P-violating electroweak interaction, H_{PV}, is added to the P-invariant part of the Hamiltonian H_0, we have an asymmetric double well potential and $\langle R|H_{PV}|R\rangle = -\langle L|H_{PV}|L\rangle \equiv \epsilon_{PV}$, the PVED between the enantiomers being $|H_{LL} - H_{RR}| = |2\epsilon_{PV}|$ [1]. In the

* Corresponding author.
E-mail addresses: igonzalo@fis.ucm.es (I. Gonzalo), pbdr@imaff.cfmac.csic.es (P. Bargueño), rpt@imaff.cfmac.csic.es (R.P. de Tudela), s.miret@imaff.cfmac.csic.es (S. Miret-Artés).

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two-state model, the eigenstates, $|\pm\rangle$, are then given by unbalanced superpositions of the chiral $|L\rangle$ and $|R\rangle$ states as,

$$\begin{pmatrix} |+\rangle \\ |-\rangle \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} |L\rangle \\ |R\rangle \end{pmatrix}, \tag{1}$$

where θ, obtained from the knowledge of the eigenvectors of $H = H_0 + H_{PV}$, is given by

$$\tan 2\theta = \frac{2H_{LR}}{H_{RR} - H_{LL}} = \frac{\delta}{\epsilon_{PV}}, \tag{2}$$

where $\delta = \langle L|H^0|R\rangle$ is related to the height of the barrier of the double well potential and determines the inversion time by tunneling between L and R enantiomers, $t_i = \hbar\pi/2\delta$. The eigenvalues are given by $E_\pm = E_0 \mp \sqrt{\epsilon_{PV}^2 + \delta^2}$, with $E_0 = (H_{LL} + H_{RR})/2$.

Following Ref. [20] we consider a canonical ensemble of non interacting chiral molecules at temperature T described by the density matrix

$$\rho_\beta = Z^{-1} e^{-\beta H}, \tag{3}$$

where $\beta = 1/(k_B T)$ and Z is the partition function. We are interested in the population difference between $|L\rangle$ and $|R\rangle$ states in thermal equilibrium at a given T. As is shown in [20], it is given by

$$n_L - n_R \equiv \langle L|\rho|L\rangle_\beta - \langle R|\rho|R\rangle_\beta = \frac{\epsilon_{PV}}{\sqrt{\epsilon_{PV}^2 + \delta^2}} \tanh\beta\sqrt{\epsilon_{PV}^2 + \delta^2}, \tag{4}$$

which is easily obtained by expressing the chiral states as linear combinations of the $|\pm\rangle$ states according to Eq. (1). Let us note that $\epsilon_{PV}/\sqrt{\epsilon_{PV}^2 + \delta^2} = \cos 2\theta$, which is the population difference at $T = 0$. The functional expression of Eq. (4) presents an inflection point at a critical temperature, T_c, which verifies $\beta_c\sqrt{\epsilon_{PV}^2 + \delta^2} \tanh\beta_c\sqrt{\epsilon_{PV}^2 + \delta^2} = 1$ [with $\beta_c = 1/(k_B T_c)$] [20], and it is given by

$$T_c \approx \sqrt{(\delta^2 + \epsilon_{PV}^2)}/(1.2\,k_B). \tag{5}$$

Around and below this temperature, the inversion by tunnel (determined by δ) and the PVED (determined by ϵ_{PV}) are not masked by thermal effects and compete between them to give place to a population difference $n_L - n_R$ governed by the ratio δ/ϵ_{PV} according to Eq. (4) and in consequence, to an enantiomeric excess in the sample.

Let us now consider the precision of the ultrasensitive polarimeter for a gas-phase sample, based on the cavity ring-down polarimetry technique [21–24]. It has a length of 129 cm, where thanks to the hundred or thousands round-trip passes of the pulse light through the cavity, an effective sample path length of 1 km can be easily achieved. The minimum optical rotation that can be detected at the end of the polarimeter is around 2.5×10^{-7} degrees $\times 129$ cm [21], i.e., 3.2×10^{-5} rotation degrees of the polarization plane of light after the light pulse has travelled through the sample an effective total path length of about 1 km, which means 3.2×10^{-10} rotation degrees in 1 cm single path length of the light through the sample. This type of ultrasensitive polarimeter is the object of a very active research trying to improve the precision.

We are now to determine the minimum value for the population difference $|n_L - n_R|$ necessary to detect a polarization rotation in this type of polarimeter. Typical values for the specific rotations $[\alpha]$ of chiral molecules are between 10 and more than 100° (rotated angle for a path length of 10 cm in a sample concentration of 1 gr cm^{-3}). Let us consider the less favorable case $[\alpha] \sim 10°$ which means that in 1 cm path length, the rotation, that we call ϕ_r, is $\phi_r \approx 1$ degrees for a concentration of 1 gr cm^{-3} of chiral molecules of one type of enantiomer, L or R. If we have N_L molecules cm^{-3} of type L and N_R cm^{-3} of type R, the rotation, ϕ, induced by the enantiomeric difference $N_L - N_R$ in 1 cm single path length is given by $\phi = [(N_L - N_R)/N_A]M\phi_r$ where N_A is the Avogadro number and M is the molar mass of the molecular compound. Since the difference $n_L - n_R$ is the enantiomeric difference per molecule, we have $(N_L - N_R) = N(n_L - n_R)$ (with $N = N_L + N_R$) and then

$$n_L - n_R = \frac{N_A\phi}{NM\phi_r}. \tag{6}$$

Assuming, for example, ambient conditions in the polarimeter, it corresponds to $N = 2.4 \times 10^{19}$ cm^{-3}. If the minimum value of ϕ is $\phi = 3.2 \times 10^{-10}$ degrees (in 1 cm of a single path length of light through the sample, as was said), and we consider $\phi_r = 1°$ for the molecule chosen, with M being in the range 50–260 for the suitable molecules (see below), then Eq. (6) yields a value for $|n_L - n_R|$ in the range 10^{-7} to 10^{-8}. We choose, for the analysis that follows, the less favorable case, i.e., $|n_L - n_R| \sim 10^{-7}$.

From Eq. (4), it is easy to see that the population difference in thermal equilibrium at room temperature is much lower than 10^{-8} since $kT \gg \sqrt{\delta^2 + \epsilon_{PV}^2}$ for all the known chiral molecules. Hence, the sample must reach a limit temperature, T_l, low enough so that the combined effect of tunneling due to δ, parity-violating energy ϵ_{PV}, and thermal equilibrium, yields a value at least $|n_L - n_R| \sim 10^{-7}$. In order to determine the limit temperature T_l, several cases must be considered from the expression (4):

(a) T_l is close to the critical temperature T_c ($T_l \approx T_c$). Then, from Eqs. (5) and (4), we obtain

$$kT_l \approx kT_c \sim 10^7|\epsilon_{PV}| \sim \delta. \tag{7}$$

Among all the chiral molecules with theoretical values of δ and ϵ_{PV} reported in the review made by Quack et al. [9], those that verify approximately the relation (7) give extremely low values for T_l, of the order of 10^{-5} K or lower, i.e., ultracold regime difficult to achieve for polyatomic molecules.

(b) $kT_l > \sqrt{\delta^2 + \epsilon_{PV}^2}$ so that the approximation $\tanh\left(\beta\sqrt{\epsilon_{PV}^2 + \delta^2}\right) \approx \left(\beta\sqrt{\epsilon_{PV}^2 + \delta^2}\right)$ can be made in Eq. (4) which becomes

$$n_L - n_R \approx \frac{\epsilon_{PV}}{kT_l} \tag{8}$$

from which we obtain

$$kT_l \sim 10^7|\epsilon_{PV}| > \delta. \tag{9}$$

Among the chiral molecules reported in [9], those verifying Eq. (9) having the highest values of ϵ_{PV} to give the highest T_l values are H_2Se_2, D_2Se_2, T_2Se_2, all of them giving $T_l \sim 3$ mK, having tunneling times $t_i = 16$ μs, 5 ms, 42 s respectively; and H_2Te_2, D_2Te_2, T_2Te_2 these ones giving $T_l \sim 40$ mK, having tunneling times $t_i = 0.55$ ms, 16 s, 5500 s respectively.

(c) $kT_l < \sqrt{\delta^2 + \epsilon_{PV}^2}$ so that $\tanh\left(\beta\sqrt{\epsilon_{PV}^2 + \delta^2}\right) \to 1$ in the expression (4) which becomes

$$n_L - n_R \approx \frac{\epsilon_{PV}}{\delta}, \tag{10}$$

and then we have

$$kT_l < 10^7|\epsilon_{PV}| \sim \delta, \tag{11}$$

which is verified by the same molecules verifying the condition (7) of case (a) but here with still lower limit temperatures.

We have then found that the most suitable molecules to detect the PVED, that is, those with higher limit temperature T_l, belong to the case (b), with $T_l \sim 3-40$ mK which lies in the cold regime. In the case that more favorable conditions than those here considered could be possible, as higher pressure in the polarimeter, higher value for the specific rotation and heavy molecules, the minimum required $|n_L - n_R|$ could be easily close to 10^{-9} giving T_l of few K.

We point out that temperatures of the order of mK and even colder have been reached within the actual experimental capabilities only for diatomic molecules and smaller systems. However, the rapid expansion of the research field on cold and ultracold chemistry is already opening new and exciting possibilities concerning polyatomic molecules showing that it may be possible to obtain cold or ultracold polyatomic molecules [19].

Now it is important to remark that since the potential barrier of the double well is high enough, the interchange between L and R conformations takes place by tunneling, the probability by surpassing the barrier being negligible. The population difference at thermal equilibrium given by (4) involves tunneling and thanks to it, the distribution between L and R conformations takes place in competition with ϵ_{PV} and kT. However, tunneling can be suppressed if the time between molecular collisions, t_c, is much shorter than the inversion time through tunneling, t_i, since, as it is known, the rapid collisions destroy the coherence of both, the superpositions states $|\pm\rangle$ and tunneling, the last one being inhibited and the L and R conformations stabilized [12,25–28]. For the tunneling times here reported, the corresponding molecules would have tunneling suppressed at the polarimeter work conditions. The importance of tunneling is then crucial as we show in the following possible situations:

(i) If the molecular compound is synthesized at temperature higher than T_l, it is necessary that when the temperature of the sample descends until T_l, tunneling takes place in order to reach the equilibrium given by Eq. (4). It is then necessary that $t_c \gg t_i$, i.e., very low density, which would be possible in highly diluted molecular beams as discussed in [14]. Only in this case the population difference given by Eq. (4) (and then the enantiomeric excess) would appear. Hence, the most favorable molecules are those with short enough tunneling times. Among the molecules mentioned in case (b), the most favorable is H_2Se_2 with $t_i = 16$ μs.
Or, once the required population difference $|n_L - n_R|$ is obtained at T_l, it must be maintained at the polarimeter work conditions. The only possibility is to inhibit tunneling at T_l. It can be done by increasing the density (and then the frequency of collisions, as said) maintaining the cold regime at T_l, or by means of a non resonant radiation with particular conditions to induce a coherent suppression of tunneling [29–31]. With tunneling suppressed, the sample can reach the polarimeter work conditions keeping the population difference reached at T_l.

(ii) If the molecular compound could be synthesized at the low temperature T_l, the corresponding population difference given by Eq. (4) would appear even in the case that tunneling is suppressed by collisions at that temperature. It is then convenient that this would be the case since, with tunneling suppressed by collisions, the sample will maintain the value of $n_l - n_R$ when it reaches the polarimeter work conditions. The most favorable molecules for such a process are those with long enough tunneling times so that the time between collisions verifies $t_c \ll t_i$. Among the molecules mentioned in case (b), the most favorable are D_2Te_2 with $t_i = 16$ s and T_2Te_2 with $t_i = 5500$ s.

In summary, we have found that for some chiral compounds in thermal equilibrium at a limit low enough temperature, $T_l \sim 3-40$ mK (or close to a few K in favorable conditions), the competition between parity-violating effects, tunneling between the two enantiomers and thermal effects, leads to a population difference between enantiomers which could be measured by means of an optical rotation experiment performed by a type of cavity ring-down ultrasensitive polarimeter, the rotation measured being then directly related with the parity-violating energy ϵ_{PV} as is expressed by Eq. (4). Once the enantiomeric difference required is obtained at low temperatures, the suppression of tunneling (possible by means of particular mechanisms) would permit that this difference is maintained at the polarimeter work conditions. Among all the known chiral molecules, those which are suitable to perform this proposal could be, H_2Se_2 (tunneling working in the cold regime), and T_2Se_2, D_2Te_2 and T_2Te_2 (if they could be synthesized at such a cold regime). We then highlight the importance of the current research in cold molecules and we urge on the experimental achieving of cold polyatomic molecules in order to detect the parity symmetry breaking at molecular level.

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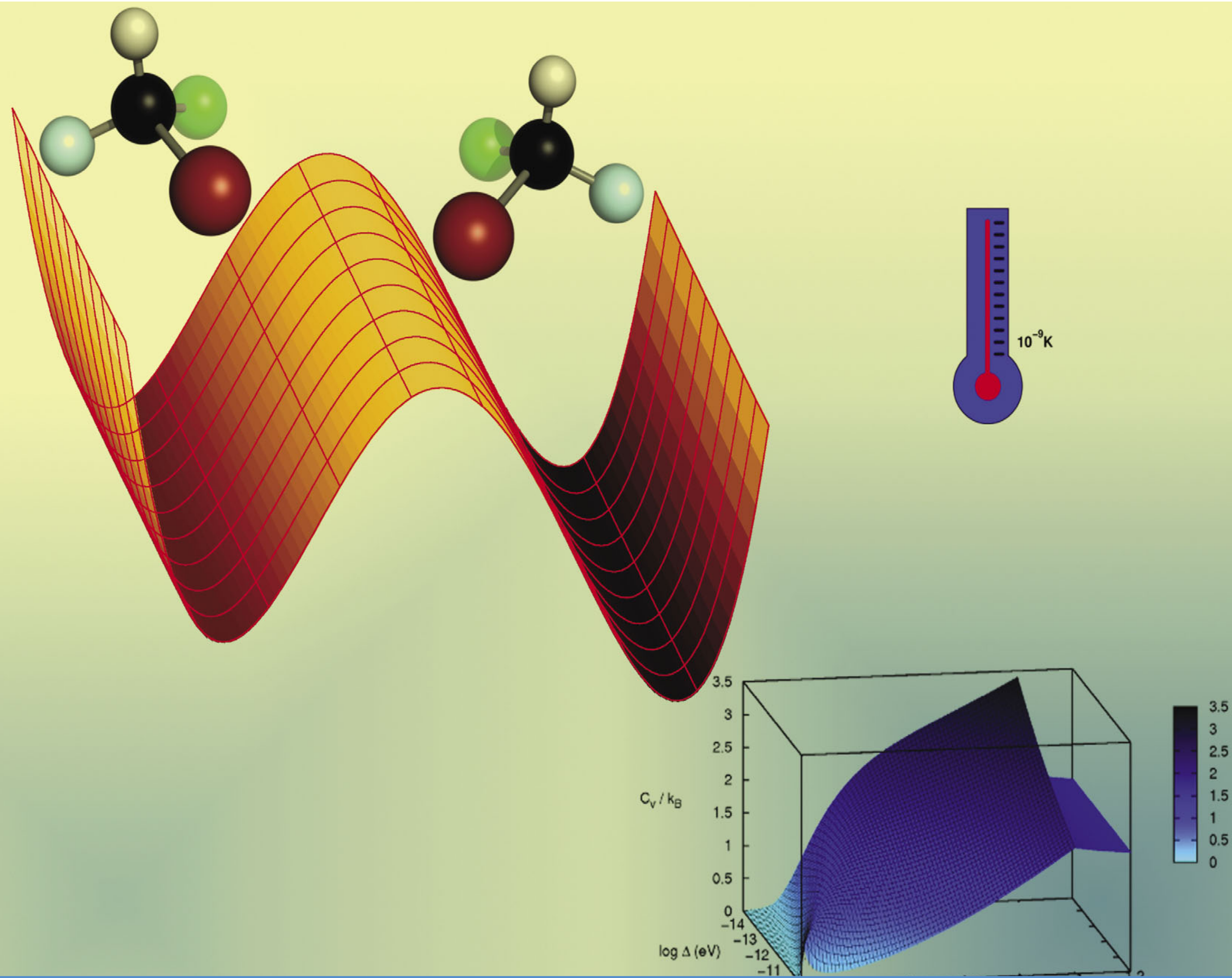

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COVER ARTICLE
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An alternative route to detect parity violating energy differences through Bose–Einstein condensation of chiral molecules

Pedro Bargueño,*[ab] Ricardo Pérez de Tudela,[a] Salvador Miret-Artés[a] and Isabel Gonzalo[c]

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Interactions which do not conserve parity might influence chiral compounds giving rise to a parity violating energy difference (PVED) that might have affected the evolution towards homochirality. However, this tiny effect predicted by electroweak-quantum chemistry calculations is easily masked by thermal effects, making it desirable to reach cold regimes in the laboratory. As an alternative route to the detection of the PVED, we study a simplified model of Bose–Einstein condensation of a sample of non-interacting chiral molecules, showing that it leads to a nonzero optical activity of the condensate and also to a subcritical temperature in the heat capacity, due to the internal structure of the molecule characterized by tunneling and parity violation. This predicted singular behavior found for the specific heat, below the condensation temperature, might shed some light on the existence of the thus far elusive PVED between enantiomers.

1. Introduction

Since the prediction and subsequent discovery of parity violation[1,2] in weak interactions, the role of discrete symmetry breaking in physics and chemistry is an intriguing field of research. Although the weak interaction (between electrons and nuclei) mediated by the gauge Z^0 boson has been extensively studied and observed in atoms,[3] it has only been predicted in molecules. In molecular systems, the theory of electroweak interactions predicts a parity violating energy difference (PVED) between the two enantiomers of chiral molecules to be between 10^{-13} and 10^{-21} eV, including polypeptides, RNA and DNA molecules.[4–14] However, no conclusive energy difference has been reported, for example, in experimental spectroscopic studies of the CHBrClF molecule reaching an energy resolution of about 10^{-15} eV.[15,16]

The importance of this symmetry-breaking in molecules is twofold: (i) at a fundamental level, the intrinsic chiral nature which is present in some molecules should reflect the underlying interaction containing pseudoscalar magnitudes such as those appearing in the weak interaction; and (ii) it could be intimately related to the origin of homochirality, that is, the almost exclusive one-handedness of the chiral molecules found in living systems, *e.g.* L-amino acids and D-sugars, this being one of the most fascinating open problems which links fundamental physics with the biochemistry of life.[17] We note that, although the PVED has been proposed to tip the balance away from racemic mixtures toward an enhancement that could be incorporated into primitive forms of life, this energy difference is extremely small, so that amplification of some sort would be required to produce a detectable effect at a macroscopic level. However, in a recent work, MacDermott and coworkers[18] conclude that parity-violation does indeed favour the neutral L form of the α-methyl amino acids found to show L-excesses in the Murchison meteorite.

But although the PVED could play some role in the evolution to homochirality, there is a problem concerning its detection due to the fact that the tiny parity violating signals are easily masked by thermal effects, thus making it highly desirable to reach cold or ultracold regimes in the laboratory.[19–22] The measurement of fundamental physical properties such as the PVED between enantiomers could be achieved by trapping molecules at low temperatures (in the milliKelvin range or below) and, subsequently, performing ultrahigh-resolution spectroscopic measurements of vibrational or electronic transitions. We would like to point out that these temperatures, and even colder, have been reached within the actual experimental capabilities only for atoms and diatomic molecules. The rapid expansion of the research field of ultracold chemistry is already opening new and exciting possibilities concerning more complex systems.[23] Thus, the study of quantum thermal effects in chiral molecules through pseudoscalar operators as the basic object describing their thermodynamics is of fundamental importance. Very recently, we have studied the corresponding classical thermodynamics of non-interacting chiral molecules.[24,25] In this sense, as pointed out by Flambaum and coworkers concerning some capabilities of Bose–Einstein condensates to amplify weak interactions in chiral molecules,[19] the study of Bose–Einstein condensation (BEC) for a gas of chiral molecules could shed some light on some properties relevant to determine the thus far elusive PVED.

Concerning this Bose–Einstein amplification of weak interactions, Salam proposed that the existence of the PVED, together with a type of BEC phenomenon, may lead to a second-order phase transition below a critical temperature allowing D-aminoacids (the less stable) to tunnel into the more stable one.[26,27] This temperature was identified with that of the

[a] *Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain. E-mail: pbdr@iff.csic.es*
[b] *Departamento de Química Física, Universidad de Salamanca, 37008 Salamanca, Spain*
[c] *Departamento de Óptica, Universidad Complutense de Madrid, 28040 Madrid, Spain*

Bardeen, Cooper and Schrieffer theory of superconductivity and was supposed to lie close to 250 K. Although recent extensive experimental studies have been devoted to test Salam's hypothesis,[28] it is generally accepted that this phase transition is kinetically hindered and a Bose–Einstein condensation of this kind is not expected to take place in the solid state.[29] However, the capability of BEC to amplify quantum effects to the macroscopic scale could be useful to detect the PVED, at least in the gas phase.

In this sense, for a Bose gas of chiral molecules, the inclusion of extra information about the internal structure of such molecules could determine some macroscopic properties relevant to obtain the PVED such as, for example, the optical activity and heat capacity (the study of cold atoms with intrinsic spin structure is currently a very hot topic, including two-component condensates, spinor condensates, *etc.*[30]). To this end, we will employ a two-state model which includes tunneling and parity violating effects in chiral molecules (this approach was first considered in ref. 31 and is widely used to describe, for instance, the internal dynamics of chiral molecules). Although the two-state (or spin 1/2) model is well known in many fields, including spin tunneling, magnetization, and quantum dissipative systems, to name only a few, this is the first time, to the best of our knowledge, that this model has been employed to study BEC of chiral molecules. Following the seminal works on BEC, predicted for a non-interacting gas and carried out in numerous dilute atomic gases[32] and in some diatomic molecules, such as $^{40}K_2$,[33] we will assume that the interaction among molecules is negligible to first order and, therefore, a non-interacting quantum gas of chiral molecules will be considered. We point out that although we are aware of the importance of interparticle interactions to study the thermodynamics at ultracold temperatures, our approach of non-interacting bosons constitutes the zeroth-order approach and retains the essential characteristics of the imprint of chirality in BEC. The very low densities needed to achieve BEC with chiral molecules tend to reduce the interaction among them.

In this article we show that a condensed gas of non-interacting chiral molecules displays optical activity related to the PVED. In addition, we show a dramatic change of the heat capacity with temperature, leading to the appearance of a secondary maximum (developing a shoulder-type-structure) associated with the Schottky anomaly below the condensation temperature. This *subcritical* temperature is expected to lie in the cold or ultracold regime.

In an ideal Bose–Einstein gas, only the translational part of the molecular motion is involved and the critical temperature for BEC is reached when the fugacity of the gas $z = \exp(\beta\mu)$, with μ being the chemical potential and $\beta = (k_B T)^{-1}$, is approaching unity (assuming that the energy of the ground state is zero).[34] This T_c depends on the molecule mass and the density of the system. At $T < T_c$, there must be a non-negligible fraction of molecules in the ground state, the internal energy goes with $T^{5/2}$ and the heat capacity with $T^{3/2}$. If each chiral molecule in the condensed phase has its own internal structure, we could ask ourselves if the corresponding quantum statistics describing the thermodynamic behavior, intimately related to the PVED, can be manifested by a macroscopic effect. For this goal, a two-state model is assumed for each chiral molecule.

2. Thermodynamics of the two-state model: a brief summary

In the absence of parity violation, the dynamics of a chiral molecule is well described by a symmetric double well potential. In this case, the true stationary states of a chiral molecule are the (achiral) eigenstates of parity. The effect of including in the Hamiltonian the internal P-odd term given by the parity violating electron-nucleon electroweak interaction, H^{PV}, introduces an energy difference between the two minima of the double well potential, leading to a new set of energy eigenstates. Let us consider the total Hamiltonian of the system $H = H^0 + H^{PV}$, with H^0 including only parity conserving terms. Using a two-state model, we choose the left and right chiral states bases, $|L\rangle$ and $|R\rangle$ (localized respectively in the left and right minimum of the double well potential), in order to show clearly the parity properties of the Hamiltonian:[31]

$$H = H^0 + H^{PV} = \delta\sigma_x + \varepsilon_{PV}\sigma_z \qquad (1)$$

where $\sigma_{x,z}$ are the Pauli matrices. The eigenstates of H, $|1,2\rangle$, can be expressed as linear combinations of the chiral states by means of a rotation where the corresponding mixing angle, θ, obtained from a knowledge of the eigenvectors of H, is given by tan $2\theta = 2H_{LR}/(H_{RR} - H_{LL}) = (\delta/\varepsilon_{PV})$. The energy splitting between the two eigenstates of H^0 is $2\delta > 0$, where $\delta = \langle L|H^0|R\rangle$. This magnitude is related to the height of the barrier of the double well potential and is inversely proportional to the tunneling time. The PVED is then given by $|H_{RR} - H_{LL}| = |2\varepsilon_{PV}|$ with $\varepsilon_{PV} = \langle R|H^{PV}|R\rangle = -\langle L|H^{PV}|L\rangle$ (we remark that ε_{PV} is the eigenvalue of a pseudoscalar operator in the chiral basis). The eigenvalues of the system are given by $E_{1,2} = E_0 \mp \Delta$, with $E_0 = (H_{RR} + H_{LL})/2$ and $\Delta \equiv \sqrt{\varepsilon_{PV}^2 + \delta^2}$ (hereafter we will take $E_0 = 0$ for the sake of simplicity).

Heat capacity contribution of the internal structure

In a gas of non-interacting chiral molecules at temperature T, the inclusion of P-odd effects leads one to deal with a pseudoscalar operator for obtaining any thermodynamic variable.[24,25] Thus, for a system described by a biased double well potential, the only magnitude which, roughly speaking, distinguishes between left and right conformations is the population difference between both wells, $N_L - N_R$, which is directly related to the optical activity of the system. If X is a pseudoscalar operator, it can be shown that

$$|\langle X\rangle_{stat}| = |x|(N_L - N_R)_{stat}, \qquad (2)$$

where $\pm x$ are the eigenvalues of X and the subscript *stat* stands for the different statistics considered. Eqn (2) is a generalization to any statistics of the Maxwell–Boltzmann (MB) thermal average.[24] If $N_{1,2}$ is the number of particles in the ground, $|1\rangle$, and the excited state, $|2\rangle$, respectively, a straightforward calculation gives the expression for $N_2 - N_1$ to be

$$(N_2 - N_1)_{\text{stat}} = \tanh \beta\Delta \left(1 + p\frac{z + z^{-1}}{2}\,\text{sech}\beta\Delta\right)^{-1}, \quad (3)$$

where $p = 0$ applies for MB, $p = -1$ for Bose–Einstein (BE) and $p = +1$ for Fermi–Dirac statistics. We remark that, when ε_{PV} dominates over δ, the true eigenstates of the system are the chiral states, $|L\rangle$ and $|R\rangle$, and changing the basis from $|1\rangle$, $|2\rangle$ to $|L\rangle$, $|R\rangle$ introduces the factor $\cos 2\theta = \varepsilon_{\text{PV}}/\Delta$ leading to

$$N_L - N_R = \varepsilon_{\text{PV}}(N_2 - N_1)/\Delta. \quad (4)$$

Moreover, $N_L - N_R$ changes its sign when considering a parity-transformed double well since ε_{PV} changes to $-\varepsilon_{\text{PV}}$. From the knowledge of $N_2 - N_1$, the internal energy of the gas is

$$U = -\Delta(N_1 - N_2)_{\text{stat}}. \quad (5)$$

From eqn (5) one can inmediately obtain the heat capacity at constant volume. This C_v can be interpreted as a measure of the fluctuations of the optical activity of the system, that is, a measure of the fluctuations of the pseudoscalar character of the system.

3. Bose–Einstein gas of chiral molecules

Let us now consider BE statistics ($p = -1$) for a gas of two-state chiral molecules, that is, the Hamiltonian H includes tunneling and parity violation. The total number of particles is $N = N_1 + N_2$. Using the standard expression for the occupation numbers for Bose statistics, we get $N = N_1 + (z^{-1}\exp(\beta\Delta) - 1)^{-1}$. For our purposes, let us define a temperature T^* in which $N_1 = 0$ (all the particles are in the excited state E_2 or, in other words, the number of particles in the ground state is negligible). This definition of the condensation temperature was also pointed out in ref. 35. This leads to the condensation temperature to be determined from $T^* = \frac{2\Delta}{k_B \ln\left(1+\frac{1}{N}\right)}$.

For $T < T^*$ it is easy to see that the gas displays a non-zero optical activity which is proportional to

$$N_1 - N_2 = N\left(1 - 2\frac{\exp(2\beta^*\Delta) - 1}{\exp(2\beta\Delta) - 1}\right). \quad (6)$$

This enables us to write:

$$\frac{N_1}{N} = 1 - \frac{\exp(2\beta^*\Delta) - 1}{\exp(2\beta\Delta) - 1}, \quad (7)$$

the average internal energy as

$$u = \frac{U}{N} = \Delta\left(2\frac{\exp(2\beta^*\Delta) - 1}{\exp(2\beta\Delta) - 1} - 1\right), \quad (8)$$

and the heat capacity as

$$C_v^{\text{int}} = \frac{\partial u}{\partial T} = 4k_B(\beta\Delta)^2\frac{\exp(2\beta^*\Delta)}{\exp(2\beta\Delta) - 1}. \quad (9)$$

It is worth noting that this heat capacity reaches its maximum value at the *subcritical* temperature, T_{sc},

$$\beta_{\text{sc}}\Delta \simeq 0.797 \quad (10)$$

which reflects nothing but the Schottky anomaly due to the saturation of the energy levels of the system. Thus, at T_{sc}, the heat capacity shows the splitting of the two levels.

Bose–Einstein condensation of a kinetic gas of two-state chiral molecules

If we include a kinetic term in the Hamiltonian, the total partition function for an ideal Bose gas of chiral molecules in the two-state model can be written as

$$Z_{\text{tot}} = Z_{\text{kin}} \cdot Z_{\text{int}} \quad (11)$$

where the subscripts denote the kinetic and internal contributions, respectively. The first factor can be found in any standard textbook of statistical mechanics[34] and the second factor is given, for our case, by

$$Z_{\text{int}} = \prod_{i=1,2}(1 - ze^{-\beta E_i})^{-1}. \quad (12)$$

The factorization of the partition function leads to a sum of the corresponding heat capacities, $C_v^{\text{tot}} = C_v^{\text{kin}} + C_v^{\text{int}}$. We note that there are now two temperature regimes involved in the chiral system: (i) the temperature at which the gas undergoes BEC (T_c) and (ii) the *subcritical* temperature (T_{sc}, below T_c) where the heat capacity displays a maximum. In the case of a free gas, T_c is related to the mass and number density of the bosons but T_{sc} depends only (for the two-state model) on the energy splitting between the $|1\rangle$ and $|2\rangle$ states. Thus, for $T < T_c$, C_v^{int} is given by eqn (9) and, for $T > T_c$, the corresponding expression can be obtained from eqn (5). C_v^{kin} is the usual heat capacity for an ideal Bose gas. It is worth pointing out that the very interesting case where T_c and T_{sc} are of the same order gives rise to an appreciable change in the heat capacity, with a shoulder-type structure below T_c. This behavior is displayed in Fig. 1, where the total heat capacity is plotted in terms of the reduced temperature k_BT/Δ for the cases $T_{\text{sc}} = 0.1T_c$ (top panel) and $T_{\text{sc}} = 0.5T_c$ (bottom panel) (we have assumed $T^* = T_c$). Strictly speaking, the effect of Δ on the condensation temperature, T_c, results in a very small shift of T_c. However, this difference is so tiny that for most practical purposes, we keep T_c instead of the shifted T_c. When $T_c = T_{\text{sc}}$, the subcritical temperature corresponds to a very precise density of bosons of mass m, n_{sc}, given by

$$n_{\text{sc}} \simeq 0.178\left(\frac{m\Delta}{\hbar^2}\right)^{3/2}. \quad (13)$$

The bottom panel of Fig. 1 should be observed, for example, for the T_2Se_2 system. This system has $\varepsilon_{\text{PV}} \approx 2.5 \times 10^{-14}$ eV, $\delta \approx 5 \times 10^{-17}$ eV and the tunneling time is $\sim$40 s (see Table 2 of ref. 13). Its subcritical density, n_{sc}, is about 10^{10} cm^{-3}, which is of the order of the critical densities. Thus, in this case, the corresponding discontinuity in the heat capacity could provide us a direct and clear signal of molecular parity violation.

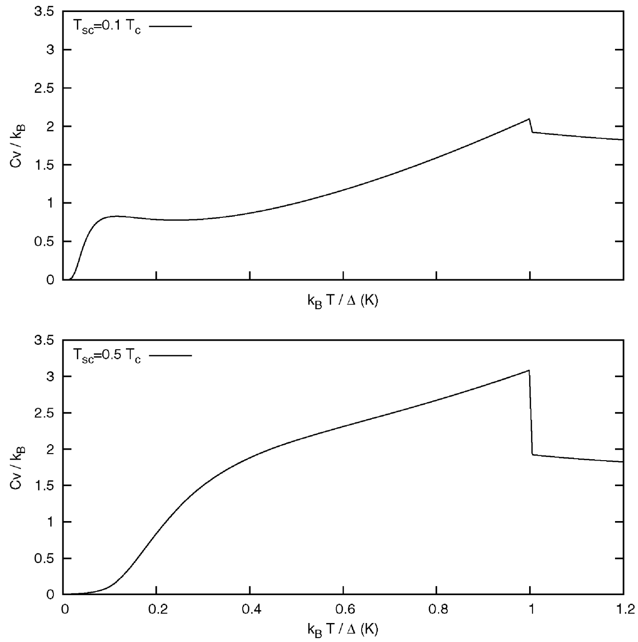

Fig. 1 Total heat capacities for a gas of chiral molecules as a function of the reduced temperature for two cases: $T_{sc} = 0.1T_c$ and $T_{sc} = 0.5T_c$. The gas undergoes BEC at $k_BT/\Delta = 1$. We have taken $T^* = T_c$. See text for symbols.

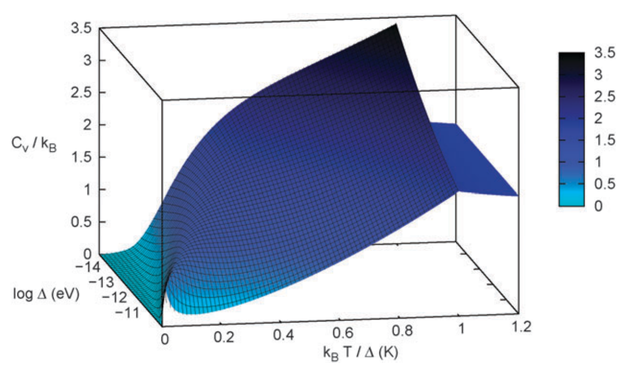

Fig. 2 Three dimensional plot of the heat capacity *versus* Δ and the reduced temperature. The gas undergoes BEC at $k_BT/\Delta = 1$. We have taken $T^* = T_c$. See text for symbols.

In Fig. 2, a three dimensional plot of the heat capacity in the range of variation [0,1.2] of the reduced temperature and [10^{-15},10^{-10}] of the splitting Δ (eV) is shown. This plot clearly shows the overall shoulder-type structure as well as the subcritical maximum for different chiral molecules, characterized by the splitting Δ. This splitting is representative of molecules such as, for example, H_2S_2, CHBrClF and H_2Se_2.[13]

4. Discussion and conclusions

The subcritical maximum (or anomalous shoulder-type structure) found here could be considered as a signal of the Schottky anomaly which comes from lifting the degeneracy of the internal degrees of freedom. Although this was previously considered in the framework of a path integral approach to study BEC in spinor gases,[36] our simple model allows us to identify the anomaly more clearly. We would like to stress that the *subcritical* temperature is determined in essence by δ and ε_{PV}, these temperatures lying in the cold or ultracold regime. The existence of such temperatures could be possible for any system whose constituents have internal ground states slightly split, such as for example: the inversion doubling of non-rigid pyramidal molecules, the splitting due to torsional or internal rotations through potential barriers in non-rigid molecules, or eventually the hyperfine structure of the ground state of atoms and molecules (in this last case, it could be more easy to verify the type of anomaly here studied). However, chiral molecules in this two-state model play a special role in BEC when the splitting is mainly due to parity violation (as in T_2Se_2). In this case, an observation of the anomaly predicted in the heat capacity provides direct information about the PVED. In addition, when ε_{PV} determines the dynamics, then the eigenstates of the system tend to be the chiral states $|L,R\rangle$. We also point out that a measurement of the optical activity of the condensate would be a confirmation of the existence of the PVED, noting that the factor ε_{PV}/Δ, which is the optical activity for zero temperature, should be measurable by state-of-the-art of actual polarimeters, as we concluded in ref. 25.

Finally, we would like to point out that the energy scale of molecular parity violation is associated with the natural scale of densities which corresponds to those achieved in Bose–Einstein condensates. Thus, BEC seems to be an alternative route to detect the PVED. Furthermore, as is well known, interactions could modify the physics of the problem, in particular by shifting the condensation temperature, so it is fundamental to ask ourselves to what extent the anomaly in the heat capacity persists when we consider an interacting system of chiral molecules. Although one could introduce the interaction between molecules under the Gross-Pitaevskii or any other more sophisticated treatment, an alternative way is to study the molecular sample as an open quantum system under the influence of dissipation. In this sense, we note that the heat capacity anomalies of open quantum systems have been recently studied when coupled to a thermal bath,[37] showing the robustness of these anomalies when the interaction is taken into account. Thus, we expect that a similar stability for the anomaly here considered will persist even in presence of an environment. The study of heat capacity anomalies in BEC chiral gases embedded in appropriately chosen environments is currently in progress.

Concerning biological chiroselection, all proposed mechanisms of discrimination between the two enantiomers, even those producing very small effects, like parity violation, are usually taken in account since several amplification processes may be present along many years. Thus, under the influence of appropriate amplification mechanisms, parity violation can not be ruled out as a possible origin of homochirality. In an attempt to provide experimental basis of the existence of this symmetry breaking effect, we have explored an alternative way to detect it through Bose–Einstein condensation.

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Quantum stochastic resonance in parity violating chiral molecules

Pedro Bargueño,[ab] Salvador Miret-Artés[a] and Isabel Gonzalo*[c]

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In order to explore parity violating effects in chiral molecules, of interest in some models of evolution towards homochirality, quantum stochastic resonance (QSR) is studied for the population difference between the two enantiomers of a chiral molecule (hence for the optical activity of the sample), under low viscous friction and in the deep quantum regime. The molecule is described by a two-state model in an asymmetric double well potential where the asymmetry is given by the known predicted parity violating energy difference (PVED) between enantiomers. In the linear response to an external driving field that lowers and rises alternatively each one of the minima of the well, a signal of QSR is predicted only in the case that the PVED is different from zero, the resonance condition being independent on tunneling between the two enantiomers. It is shown that, at resonance, the fluctuations of the first order contribution to the internal energy are zero. Due to the small value of the PVED, the resonance would occur in the ultracold regime. Some proposals concerning the external driving field are suggested.

1. Introduction

Biological homochirality, that is, the almost exclusive one-handedness of chiral molecules found in living systems (D-sugars and L-aminoacids) is one of the fundamental problems of science which still remains unsolved.[1] In the mid 1950s comes on stage the discovery that parity (P), the symmetry operation which inverts the position of all particles with respect to the origin, is violated in the weak interaction.[2,3] This interaction gives rise to the parity violating energy difference (PVED) between the two enantiomers of a chiral molecule. Given the universality of this PVED, it has been suggested as a possible origin of biological homochirality, although due to its small value, the enantioselection would have taken place through powerful mechanisms of amplification as those involving nonlinear processes in systems far from equilibrium.[4,5] Although the weak interaction has been extensively studied and observed in atoms,[6,7] it has only been predicted in molecules. Electroweak quantum chemistry calculations predict the PVED to be between 10^{-13} and 10^{-21} eV[8–11] but no conclusive energy difference has been reported, for instance, in experimental spectroscopic studies of the CHBrClF molecule reaching an energy resolution of about 10^{-15} eV.[12] It is however noticeable the experimental results of Wang *et al.*[13,14] in which a chiral discriminating phase transition without conformational changes was obtained at temperature 77–300 K for D/L-alanine and valine. It was interpreted as a manifestation of the PVED and related to the phase transition postulated by Salam.[15] It is also of interest the evidence obtained[16] of the differences in structural transitions between poly-L- and poly-D-amino acids of equal length in *ortho*-H_2O, attributed to an amplification mechanism of the PVED in the α-helix autocatalytic formation. Other kind of experiments have been proposed, based on the pioneering work of Harris and Stodolsky,[17] dealing with the electroweak optical activity of chiral molecules.[18–20] As it is well known, the parity violating signals are easily masked by thermal effects, being highly desirable to reach cold or ultracold regimes in the laboratory.[21,22] In this sense, we have studied in recent works the role of classical and quantum statistics in the thermodynamics of chiral molecules, suggesting some experiments to detect the PVED with classical[20,23] and Bose-condensed[24] gases.

In order to explore physical or chemical phenomena where the tiny PVED would manifest itself, the mechanism of the quantum stochastic resonance (QSR) in chiral molecules is here analyzed. The chiral molecule is described by a two-state system in an asymmetric double well potential coupled to a heat bath and subjected to an external periodic driving field which biases the two minima of the well alternatively. As it is known, spin-boson systems have been active object of study since the works of Leggett and coworkers,[25,26] and their application to P-violating chiral molecules is found in the pioneering works of Harris and Silbey.[27–29] However, as far as we know, the results of a driven spin-boson system has never been applied to the case of P-violating chiral molecules. We restrict our study to very low temperatures where deep quantum tunneling is the only mechanism for barrier crossing. In this regime, QSR has been studied and various novel phenomena predicted.[30–32] Following such previous works, it is shown that for low viscous friction, and in the linear response regime, QSR in the optical activity of the sample is predicted only when there is a non-zero PVED; the condition of resonance being independent of tunneling. We also interpret the resonance conditions in terms of the fluctuations of the internal energy. Finally, the characteristics of the driving field are discussed.

[a] *Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain. E-mail: pbdr@iff.csic.es*
[b] *Departamento de Química Física, Universidad de Salamanca, 37008 Salamanca, Spain*
[c] *Departamento de Óptica, Facultad de Ciencias Físicas, Universidad Complutense de Madrid, 28040 Madrid, Spain. E-mail: igonzalo@fis.ucm.es*

2. Characterization and interpretation of QSR in chiral molecules

We consider a two-level system in an asymmetric double well potential where the PVED is the static energy difference between the two minima. The system is coupled to a bath of harmonic oscillators by means of a bilinear interaction in the system-bath coordinates. An external harmonic force rises and lowers in an alternate way each one of the two minima of the well. Then, in the localized basis, $|L\rangle$, $|R\rangle$, of the molecule, the driven spin-boson Hamiltonian reads ($\hbar = 1$)[26]

$$H = -\frac{1}{2}\delta\sigma_x - \frac{1}{2}(\varepsilon_{\mathrm{PV}} + \varepsilon\cos(\Omega t))\sigma_z + \frac{1}{2}\sum_j\left(\frac{p_j^2}{m_j} + m_j\omega_j^2x_j^2 - c_jx_ja\sigma_z\right), \tag{1}$$

where $\sigma_{x,z}$ are the Pauli matrices, δ is the tunneling splitting between the eigenstates of the symmetric double well, $\varepsilon_{\mathrm{PV}}$ is the PVED between L and R enantiomers, $\varepsilon\cos(\Omega t)$ is the interaction energy of the molecule with the periodic external field of frequency Ω, x_j are the coordinates of the bath oscillators of frequency ω_j, a is the distance between the two minima of the double well and c_j are coupling constants. As it is known, the eigenstates $|1\rangle$ (lower), $|2\rangle$ (upper) of the isolated asymmetric molecular system have the energy eigenvalues $E_{1,2}(t) = \mp\Delta(t)$ when an appropriate energy origin is chosen, with $\Delta(t) \equiv [\varepsilon_{\mathrm{PV}}^2 + \varepsilon^2(t) + \delta^2]^{1/2}$. For the spectral density of the environment, $J(\omega)$, Ohmic dissipation $J(\omega) = (2\pi/a^2)\alpha\omega e^{-\omega/\omega_c}$ is assumed, where ω_c is a cutoff frequency[25,26] and α is the dimensionless coupling strength quantifying the viscous friction. It will be taken $\alpha = 1/2$ to exploit the full analicity of this case.[31] We focus on the dynamical quantity of interest

$$P(t) \equiv \langle\sigma_z(t)\rangle_{QS} = n_L(t) - n_R(t)$$

where $n_{L,R}$ are the respective population of the molecules in L and R conformations. Such a population difference is proportional to the optical activity of the sample. As usual, $\langle\ldots\rangle_{QS}$ involves quantum statistical average over the bath degrees of freedom. As is known, for times t large compared to the time scale of the transient dynamics, the asymptotic value of $P(t)$ can be expressed as[30]

$$P_{\mathrm{as}}(t) = \sum_{m=-\infty}^{\infty} P^{(m)}(\Omega,\varepsilon)e^{-im\Omega t}. \tag{2}$$

The square amplitudes $|P^{(m)}|^2$ are directly related to the intensities of the δ-spikes of the power spectrum. The scaled spectral amplification in the mth frequency is given by η_m which is proportional to the ratio $|P^{(m)}/\varepsilon|^2$. Furthermore, other magnitudes derived from P_{as} also display the same behavior with time as, for instance, the internal energy U_{as} and the specific heat $C_{v,\mathrm{as}}$:

$$U_{\mathrm{as}}(t) = \sum_{m=-\infty}^{\infty} U^{(m)}(\Omega,\varepsilon)e^{-im\Omega t}, \tag{3}$$

$$C_{v,\mathrm{as}}(t) = \sum_{m=-\infty}^{\infty} C_v^{(m)}(\Omega,\varepsilon)e^{-im\Omega t}, \tag{4}$$

where $C_v^{(m)} = \partial U^{(m)}/\partial T$.

In the linear response regime, which is the appropriate regime to study the tiny P-odd effect predicted, only the first two contributions, $m = 0$ and $m = \pm1$ of $P_{\mathrm{as}}(t)$ are important. Following the standard procedure,[26] we have for the zeroth-order (in the absence of driving) contribution,

$$P^{(0)} \equiv \langle\sigma_z\rangle_{QS}^{(0)} = \frac{\varepsilon_{\mathrm{PV}}}{\Delta_0}\tanh\beta\frac{\Delta_0}{2}, \tag{5}$$

where $\Delta_0 \equiv \sqrt{\delta^2 + \varepsilon_{\mathrm{PV}}^2}$ and $\beta = 1/(k_{\mathrm{B}}T)$ with T the temperature and k_{B} the Boltzman constant. The non-zero optical activity derived from this result is due to the PVED between enantiomers, $\varepsilon_{\mathrm{PV}}$. Eqn (5) gives the population difference in thermal equilibrium without external driving field, that we have already obtained and discussed in a previous work.[23] It was deduced that the internal energy $U^{(0)} = -(\Delta_0/2)\tanh(\beta\Delta_0/2)$, and using eqn (5), it can be reexpressed as

$$U^{(0)} = -\frac{\Delta_0^2}{\varepsilon_{\mathrm{PV}}}P^{(0)}. \tag{6}$$

We note at this point that from the specific heat $C_v^{(0)} = \partial U^{(0)}/\partial T$ and the condition $\partial C_v^{(0)}/\partial T = 0$, a critical temperature, T_c, is defined to be[23]

$$\beta_c\frac{\Delta_0}{2}\tanh\beta_c\frac{\Delta_0}{2} = 1, \tag{7}$$

which is interpreted as the temperature which separates the region in which tunneling and parity violation compete with thermal effects.

Now we focus on $P^{(1)}$ which is related, by Kubo's formula,[33] to the linear susceptibility of the system. Following the standard procedure exposed, for example, in Weiss's book,[26] assuming low viscous friction and the restrictions $\Omega\beta \ll 1$, $\varepsilon\beta \ll 1$ and $\varepsilon < \varepsilon_{\mathrm{PV}}$, the first-order contribution of the response of our system to the external amplitude ε is expressed as

$$P^{(1)} \equiv \langle\sigma_z\rangle_{QS}^{(1)} = \varepsilon\hat{\chi}(\Omega) = \frac{\varepsilon}{4}\frac{\lambda^2}{\lambda^2+\Omega^2}f(\beta,\varepsilon_{\mathrm{PV}}), \tag{8}$$

where

$$f(\beta,\varepsilon_{\mathrm{PV}}) = \beta\,\mathrm{sech}^2\beta\frac{\varepsilon_{\mathrm{PV}}}{2} \tag{9}$$

and, for Ohmic dissipation and $\alpha = 1/2$, we have $\lambda = \pi\Delta_0^2/(2\omega_c)$.

Thus, from eqn (5), (8) and (9), the asymptotic limit of the population difference $P(t)$, up to first order in the energy of the coupling to the external field, is given by

$$P_{\mathrm{as}}(t) = \frac{\varepsilon_{\mathrm{PV}}}{\Delta_0}\tanh\beta\frac{\Delta_0}{2} + \frac{\varepsilon}{2}\beta\,\mathrm{sech}^2\left(\beta\frac{\varepsilon_{\mathrm{PV}}}{2}\right)\frac{\lambda^2}{\lambda^2+\Omega^2}\cos(\Omega t). \tag{10}$$

provided $\varepsilon,\Omega \ll kT_{\mathrm{B}}$ and $\varepsilon < \varepsilon_{\mathrm{PV}}$.

It is easy to see that the spectral amplification, given by η_1, displays a maximum with respect to the temperature, this being the signal of QSR. The temperature at which the maximum occurs, the quantum stochastic temperature, T_{st}, is obtained from the condition $\partial P^{(1)}/\partial T = 0$, which reads

$$\beta_{st}\varepsilon_{PV} \tanh \beta_{st}\frac{\varepsilon_{PV}}{2} = 1, \quad (11)$$

or

$$k_B T_{st} \approx 0.65\varepsilon_{PV}, \quad (12)$$

which is in quantitative accord with the fact that $k_B T_{st}$ is of the order of the static asymmetry.[30] We note the similarity between eqn (7) and (11), pointing out that the main difference between T_c and T_{st} is that the former depends on δ and ε_{PV}, whereas the latter only depends on ε_{PV}. The existence of ε_{PV}, that is, of the PVED between enantiomers, could then be manifested through the existence of the QSR in the population difference between enantiomers, that is, in the optical activity of the sample, since the maximum of $P^{(1)}$ disappears for $\varepsilon_{PV} = 0$. In Fig. 1, the amplification, $P^{(1)}/\varepsilon$, is plotted as a function of the temperature and ε_{PV}, in a range of ε_{PV} values around 10^{-14} eV, and taking the factor $\lambda^2/(\lambda^2 + \Omega^2)$ as unity. It is seen from Fig. 1 that the maximum increases as ε_{PV} decreases. However, when ε_{PV} increases, the position of the maximum is shifted to higher temperatures but with a smaller amplification. In any case, given the small value predicted for ε_{PV}, the maximum lies in the very deep ultracold regime ($\sim 10^{-10}$ K in the Figure). We remark that the QSR arises only for low viscous friction in the presence of a non-zero ε_{PV}, the condition of the maximum being independent of the tunneling value.

Concerning the internal energy, we now proceed in an analogous way to that followed for the zeroth-order contribution. Thus, the first-order contribution to the internal energy $U^{(1)}$ can be expressed as

$$U^{(1)} = -\frac{\Delta_0^2}{\varepsilon_{PV}} P^{(1)}, \quad (13)$$

resulting into the first-order heat capacity $C_v^{(1)} = \partial U^{(1)}/\partial T$, given by

$$C_v^{(1)} = -\frac{\Delta_0^2}{\varepsilon_{PV}}\frac{\partial P^{(1)}}{\partial T}. \quad (14)$$

Thus, the conditions where there is a maximum in $P^{(1)}$ are equivalent to the conditions where $C_v^{(1)} = 0$. Hence, QSR

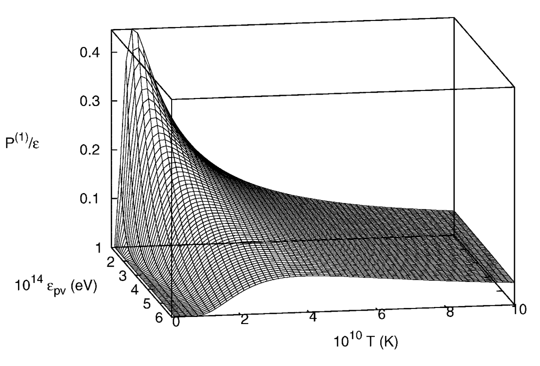

Fig. 1 Amplification $P^{(1)}/\varepsilon$ *versus* temperature T of the order of 10^{-10} K, and *versus* ε_{PV} of the order of 10^{-14} eV is plotted to show the quantum stochastic resonance in chiral molecules (see the text).

Table 1 ε_{PV}, δ, T_c and T_{st} are shown for some selected molecules. The orders of magnitude of ε_{PV} and δ have been taken from the review of Quack[10]

Molecule	ε_{PV}/eV	δ/eV	T_c/K	T_{st}/K
H_2O_2	10^{-18}	10^{-4}	1	10^{-14}
H_2S_2	10^{-16}	10^{-10}	10^{-6}	10^{-12}
H_2Te_2	10^{-13}	10^{-12}	10^{-8}	10^{-9}
CHFBrCl	10^{-16}	Very small	10^{-12}	10^{-12}

would occur at a temperature T_{st} at which there are no fluctuations in the first-order internal energy contribution and, therefore, in the population difference $P^{(1)}$. In this situation, $C_v = C_v^{(0)}$ in the linear response regime.

Table 1 shows a short list of selected chiral molecules[10] with the orders of magnitude of their corresponding temperatures T_{st} at which QSR would appear together with the critical temperatures T_c defined in eqn (7) associated with $C_v^{(0)}$.

Notice the different orders of magnitude of T_c and T_{st} in the cases where the tunneling splitting is much greater than ε_{PV}. This is due to the fact that T_{st} does not depend on δ whereas T_c does.

We must note that the two-state model here applied is valid only in the case that the energy splitting between the two levels, given by $\sqrt{\delta^2 + \varepsilon_{PV}^2}$, is much smaller than the energy of the first excited rotational level of the molecule, which is of the order of 10^{-3}–10^{-4} eV. Under this condition and for the ultracold regime, the influence of the remaining excited states can be considered negligible. Note that for a high enough δ value this condition can fail.

In order to propose an appropriate external periodic driving field, we must note that, in a non-oriented sample, only a chiral field can induce a different energy in L and R conformations of a chiral molecule. Thus, circular polarized light is a chiral field leading to opposite interaction energy values for the two enantiomers. This energy, averaged for the rapid oscillations of light, has been evaluated,[34] and found to be

$$\varepsilon = \pm\frac{16}{3}EB\omega\frac{R_{n0}}{\omega_{n0}^2 - \omega^2}, \quad (15)$$

where each sign corresponds to each one of the two enantiomers respectively, E and B are the electric and magnetic radiation field, ω_{n0} is the resonance frequency nearest the radiation frequency ω, and R_{n0} is the rotational strength of the optical activity of the molecule, which can be considered to be of the order $R_{n0} \sim 10^{-18}$. If we assume $\omega^2/(\omega_{n0} - \omega^2) \sim 1$, and the frequency of the light $\omega \sim 10^{15}$ rad s^{-1}, we obtain $\varepsilon \sim 10^{-24}E^2$ which, with lasers of about 1 W cm^{-2}, becomes $\varepsilon \sim 10^{-16}$ eV, which is in the appropriate range (lower than ε_{PV}) to study the QSR in chiral molecules. Then, the external driving field could be this type of light, but changing its circular polarization from left to right periodically with low enough frequency Ω. Since $\beta\Omega \ll 1$, and QSR is predicted in the very deep ultracold regime, it is desirable for our system that $\Omega \sim 0.1$ rad s^{-1} or less. It would permit the measurement of optical activity of the sample in a time shorter than $2\pi/\Omega$ and then the detection of the optical activity oscillations, and hence the QSR if $\varepsilon_{PV} \neq 0$. The major problem is, of course, to achieve the ultracold regime.

Another proposal, probably more difficult to implement than the previous one, would consist of an oriented sample where opposite enantiomers have their permanent dipole moments, **d**, oriented in opposite directions. Then, an external electric field **E** is able to produce an interaction energy $\pm\mathbf{E}\cdot\mathbf{d}$ of opposite sign for each enantiomer. The electric field must then oscillate periodically with frequency Ω, and the value of E must be extremely small to get an ε value smaller than ε_{PV}. The requirements for Ω and the temperature are the same as in the preceding case.

3. Conclusion

This study could be considered as a contribution to the search for the PVED in chiral molecules, of interest in some biochemical models of evolution towards the biological homochirality. For this goal, a QSR analysis has been carried out. Quantum stochastic resonance in the population difference between the two enantiomers of a chiral molecule (and then in the optical activity of the sample) has been studied for P-violating chiral molecules, in the linear response to an external driving periodic field, in the deep quantum regime and under low viscous friction. As was expected, only in the case that a parity violating energy difference between enantiomers exists, a signal of QSR is predicted in the ultracold regime. Thus, any confirmation of the existence of this signal should be an unequivocal signature for parity violation in chiral molecules. The temperature at which QSR is predicted depends only on the static asymmetry, determined by the PVED, being independent on tunneling. In resonance, not only the fluctuations of the first-order population difference are zero, but also those of the first-order contribution to the internal energy. Some proposals are made on the external driving field. It must be chiral if we deal with a non-oriented sample, for example, a light changing its circular polarization from left to right periodically with a change frequency Ω. A small value of Ω would permit optical activity measurements during the oscillations.

Concerning the major problem which is to reach the ultracold regime, we note that it has been reached within the actual experimental capabilities only for diatomic molecules and smaller systems. However, recent works[35] show that it might be possible in the near future to cool polyatomic molecules to ultralow temperatures as well.

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Constraining long-range parity violation in gravitation using high resolution spectroscopy of chiral molecules

Pedro Bargueño[1,2,*] and Ricardo Pérez de Tudela[1]

[1]*Instituto de Física Fundamental (CSIC), Serrano 123, 28006 Madrid, Spain*

[2]*Departamento de Química Física, Universidad de Salamanca, 37008 Salamanca, Spain*

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New bounds on long-range parity violation in gravitation are reported from inconclusive searches of parity violating energy differences (PVED) in chiral molecules. In particular, it is found that Leitner-Okubo-Hari Dass's α_2 (or A_2) parameter is constrained by current experimental searches of PVED between molecular enantiomers. The possibility of constraining other parameters which parametrize the strength of contact parity violation in gravity, as well as other long-range parity violating potentials will be briefly commented.

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I. INTRODUCTION

Since the prediction and subsequent discovery of parity (P) violation [1,2] in weak interactions, the role of discrete symmetries in fundamental interactions is an intriguing field of research. Correlations between this lack of symmetry in the weak interaction and its corresponding weakness led Leitner and Okubo to inquire whether or not gravitation would share this kind of symmetry violation [3]. In [3], the authors proposed a P-odd long-range gravitational potential that can be generalized to include terms which violate also charge conjugation (C) and P, and C and time reversing (T) symmetries, leading to the general potential:

$$U(r) = U_0(r)\{1 + A_1\vec{\sigma}\cdot\hat{r} + A_2\vec{\sigma}\cdot\vec{v}/c + A_3\hat{r}\cdot\vec{v}/c\times\vec{\sigma}\}, \tag{1}$$

where $U_0(r)$ is the usual Newtonian potential, $U_0(r) = GMm/r$, A_1, A_2, and A_3 are dimensionless constants much smaller than one, and $\vec{\sigma}$ and $\vec{v}$ are, respectively, the spin and the velocity of the test particle which feels the gravitational field. Let us note that Eq. (1) implies also a violation of the weak equivalence principle due to the spin-dependent terms.

In addition to the generalized Leitner-Okubo parametrization, Hari Dass proposed phenomenologically a different potential [4] which we can write as

$$U(r) = \alpha_1\frac{GM\vec{s}\cdot\vec{r}}{r^3} + \alpha_2\frac{GM\vec{s}\cdot\vec{v}}{r^2} + \alpha_3\frac{GM\vec{s}\times\vec{r}\cdot\vec{v}}{r^3}, \tag{2}$$

being α_i dimensionless constants which can be easily related with A_i by $A_1 = \alpha_1/mr$, $A_2 = \alpha_2/mr$, etc. [4] (unless otherwise stated, we are considering $\hbar = c = 1$). We have to note that, as was pointed out by Hari Dass, there is a context dependent relation between the constants that parametrize the potential in Eq. (1) and in Eq. (2). Clearly, the strength of P and T, C and P, and C and T violation in the gravitational interaction (if CPT symmetry is assumed) is due, respectively, to the α_1, α_2, and α_3 terms.

There have been several attempts to estimate numerical values of these constants, looking for possible tests of discrete symmetry violations in the gravitational interaction. Thus, Leitner and Okubo estimated $A_1 \leq 10^{-11}$ (which is equivalent to $\alpha_1 \leq 10^{10}$) by using the uncertainties in the measurement of the fine structure constant in the hyperfine splitting of hydrogen [3]. Some years after that, Hari Dass proposed the first quantum mechanical experiment which, in principle, could test the validity of Eq. (2) [4–6]. This experiment is based on the existence of spin precession for elementary particles which are earth bounded, caused by the α_1 and α_2 terms and it would report, in principle, $\alpha_1 \sim 1$. In addition, concerning laboratory searches of discrete symmetry breaking in gravitation, Anandan proposed a neutron interference experiment which could also test these effects at quantum mechanical level [7]. This experiment, which has not been performed up to date, would give, under optimistic assumptions, $A_1 \leq 10^{-18}$ ($\alpha_1 \leq 10^5$) and $A_2 \leq 10^{-10}$ ($\alpha_2 \leq 10^{13}$).

Some years ago, Longo [8] and Krauss and Tremaine [9] pointed out that the measured differences in arrival times of photons and neutrinos coming from the stellar collapse in the large magellanic cloud could give a very accurate test of the equivalence principle. Their result was extended by LoSecco to test CP invariance in general relativity [10]. After that, Choudhuri, Hari Dass, and Murthy [11] estimated $\alpha_1 \leq 10^2$ from studies of gravitational helicity flip related with the cooling rate of neutron stars. Generalizing previous ideas, Almeida, Matsas, and Natale were able to obtain $A_1 \leq 10^{-3}$ and $A_2 \leq 10^{-3}$ ($\alpha_{1,2} \leq 10^{30}$) [12]. As was pointed out by the authors, their bound on A_1 was worse than Leitner and Okubo's estimation, but the corresponding bound on A_2 was the first constrain on it reported

*pbdr@imaff.cfmac.csic.es

in the literature. After that, LoSecco *et al.* estimated $A_1 \leq 2 \times 10^{-10}$ ($\alpha_1 \leq 2 \times 10^{23}$) and $A_2 \leq 6 \times 10^{-11}$ ($\alpha_2 \leq 6 \times 10^{22}$) from pulsar measurements of differences in arrival times of left and right-handed circularly polarized light [13]. Using the same method, Klein and Thorsett [14] were able to obtain, up to date, the tightest constrain on A_2 (α_2) obtained from astrophysical measurements, $A_2 \leq 10^{-12}$ ($\alpha_2 \leq 10^{21}$) (they estimated also $A_1 \leq 4 \times 10^{-12}$, which corresponds to $\alpha_1 \leq 4 \times 10^{21}$).

The most stringent limit on α_2 has been obtained by experiments with trapped ions. Any experiment that puts a limit on, say α_1, by the experimental errors on some observable, also puts a limit on α_2 though the bound is much poorer. The trapped atom experiments do put the limit $\alpha_1 \leq 70$ [15], so the corresponding limit on α_2 would be $\alpha_2 \leq 10^{11}$.

The most recent efforts are focused towards the detection of short-range spin-dependent gravitational forces. In this sense, it is also interesting to note that Dobrescu and Mociou [16] classified the kind of potentials that might arise from the exchange of low-mass bosons, constrained only by rotational and translational invariance. One of these potentials (which does not conserve P) can be written as

$$V^{\rm PV} = A_v \vec{s} \cdot \vec{v} \frac{e^{-r/\lambda}}{r}, \qquad (3)$$

where λ is the interaction cutoff and $\vec{v}$ is the relative velocity. The first bound on A_v, $A_v/\hbar c \sim 10^{-57}$, has been recently obtained by Heckel *et al.* [17] searching for P-odd interactions between $\sim 9 \times 10^{22}$ electrons of a torsion pendulum and unpolarized matter in the surroundings of the Sun. Although this potential does not refer to gravity, we will make a brief comment about the possibility of obtaining bounds on A_v from our method.

In this work, in an attempt to get more insight from quantum mechanical laboratory experiments, we will test long-range P violation in gravitation using experimental searches of parity violating signatures in chiral molecules. Our estimations will be based in the existence of parity violating energy differences (PVED) between different molecular enantiomers, due to helicity-type terms which appear in the usual electroweak Hamiltonian as well as in the P-odd Leitner-Okubo-Hari Dass potential. To this end, we first review briefly the main characteristics of the effective P-odd molecular potentials considered in the past, to finally establish some resemblances with the Leitner-Okubo-Hari Dass's potential. Although the entire discussion will be given in terms of α_2 rather than A_2 to get a context independent feel, some comparisons between our values of A_2 and those reported in the literature will be given for the sake of completeness.

II. ELECTROWEAK AND P-ODD GRAVITATIONAL INTERACTIONS IN CHIRAL MOLECULES

It is usually assumed that the only interaction which plays noticeable effects at the molecular level is the electromagnetic one. However, weak interactions (between electrons and nuclei) mediated by the Z^0 boson have been extensively studied and observed in atoms [18] and only predicted in molecules, where inconclusive energy differences between enantiomers have been reported within an experimental resolution of 10^{-14} eV [19–21]. Although this P-odd interaction has been related to the observed biomolecular homochirality, some enhancement mechanisms are needed to be taken into account for the tiny PVED predicted between enantiomers. Concerning the role of nonconserving P processes in the homochirality of life, neutrino-electron and dark matter (WIMP)-electron interactions have been reported in previous works [22–24].

All these P-odd interactions (electron-nuclei, electron-neutrino, and electron-WIMP) can be derived from the usual electroweak Hamiltonian density:

$$H = \frac{G_{\rm F}}{\sqrt{2}} \bar{e} \gamma^\mu (g_V - g_A \gamma_5) e \bar{\psi} \gamma_\mu (1 - \gamma_5) \psi, \qquad (4)$$

where G_F is Fermi's constant, e denotes the electron spinor field, $\bar{e}$ is its adjoint spinor, γ^μ are the Dirac matrices (regarded as a four vector), $\gamma^5 = i\gamma^0\gamma^1\gamma^2\gamma^3$, and $g_{V,A}$ are suitable coupling constants that parametrize the strength of the interactions. The nucleus (neutrino or WIMP) spinor is represented by ψ.

Considering the nonrelativistic neutrino-electron interaction, it is possible to obtain, for Dirac neutrinos, the following parity violating potential [22,25,26]:

$$V^{\rm PV}_{\nu-e} \sim \frac{G_{\rm F}}{m_e} (n_\nu - n_{\bar{\nu}}) \sum_i \vec{s}_i \cdot \vec{p}_i, \qquad (5)$$

where the sum runs over i electrons, m_e is the mass of the electron, $n_\nu - n_{\bar{\nu}}$ is the neutrino-antineutrino number density difference, and $\vec{s}_i$ and $\vec{p}_i$ are, respectively, spin and momentum operators of the molecular electron.

Let us note that there is an energy splitting between the two helicity states of an electron of a chiral molecule, because $\langle \vec{s}_e \cdot \vec{p}_e \rangle$ takes opposite sign for each molecular enantiomer (as we can see easily from a simplified chiral molecule model [22,27]).

In the case of dealing with nonrelativistic electron-nucleon interaction, the corresponding (nuclear spin-independent) potential is (see, for example, [20,28]):

$$V^{\rm PV}_{N-e} \sim \frac{G_{\rm F}}{m_e} \sum_{i,j} Q_j \{\vec{s}_i \cdot \vec{p}_i, \delta^{(3)}(\vec{r}_i)\}, \qquad (6)$$

where $\{,\}$ stands for an anticommutator, the sum runs over i electrons and j nuclei and $\vec{s}_i$ and $\vec{p}_i$ are, respectively, spin and momentum operators of the ith electron. $Q_j = Z(1 - 4\sin^2\theta_W) - N$ is the electroweak charge of the nucleus j with Z protons and N neutrons, and $\delta^{(3)}$ is the three-dimensional delta function centered in the position of the nucleus. θ_W is Weinberg's angle, usually taken as $\sin^2\theta_W \sim 0.2236$. As can be revealed by inspection of Eq. (6), in this case there is also an energy splitting (the so called PVED) when we average $V^{\rm PV}_{N-e}$ between states of opposite molecular enantiomers (see [20] for a recent review concerning the calculus and laboratory searches of these PVED).

Although at this point it is clear that the relation between the energy splitting of enantiomers between Eqs. (2), (5), and (6) is due to the operator $\vec{s}_e \cdot \vec{p}_e$, it is interesting to simplify all of them introducing the electron chirality, $\chi(x)$, defined as

$$\chi(x) = N_e \Re \sum_s \int d^3x_2 \ldots d^3x_N \psi^\dagger(x, x_2, \ldots x_N, s_1, \ldots s_N) \cdot (\vec{s}_e \cdot \vec{p}_e)\psi(x, x_2, \ldots x_N, s_1, \ldots s_N), \tag{7}$$

where N_e is the total number of electrons in the molecule, $\Re$ denotes the real part, p_e is the electron momentum operator, and ψ is the many-electron wave function with electron spatial coordinates $x_1, \ldots, x_N$ and spin coordinates $s_1, \ldots, s_N$ [29].

Thus, if $\Delta E^{\rm PV}_{\nu-e}$, $\Delta E^{\rm PV}_{N-e}$, and $\Delta E^{\rm PV}_{\alpha_2}$ are, respectively, the energy differences obtained averaging Eqs. (2), (5), and (6) over states of opposite enantiomers, we have

$$\Delta E^{\rm PV}_{\nu-e} \sim \frac{G_{\rm F}}{m_e}(n_\nu - n_{\bar{\nu}})\sum_i \chi(x_i), \tag{8}$$

$$\Delta E^{\rm PV}_{N-e} \sim \frac{G_{\rm F}}{m_e}\sum_j Q_j \chi(x_j), \tag{9}$$

$$\Delta E^{\rm PV}_{\alpha_2} = \alpha_2 \frac{GM}{r^2 m_e}\sum_i \chi(x_i). \tag{10}$$

Since our results will be based on Eqs. (9) and (10), let us note the main differences between them. The electronic chirality function, χ, which appears in the former equation, is summed over the j nuclei of the molecule and it is evaluated at each nuclei. This essential fact, due to the three-dimensional delta function which appears in Eq. (6) as a consequence of the pointlike nucleus approximation, is not present in Eq. (10). On the contrary, in the later equation, the corresponding electronic chirality is calculated at each point of the molecule.

We have to note that, although we are considering phenomenological potentials which lead to P-odd gravitational interactions of long range, there are some models which extend general relativity including also coupling of fermionic degrees of freedom to gravity in the presence of torsion. These models lead to the appearance of a P-odd contact potential similar to that shown in Eq. (6), but with an effective weak charge with value

$$Q_I = -9\pi\beta(Z + N)\frac{\sqrt{2}G_N}{G_{\rm F}}, \tag{11}$$

where $\beta = \frac{2\gamma\alpha}{\gamma^2+1}$. This constant is related to the kind of fermionic coupling ($\alpha \neq 0$ means nonminimal coupling) and to the Immirzi parameter, γ (see [30] for details). The ratio of $\sqrt{2}G_N$ to $G_{\rm F}$ is about 10^{-33}. As the authors of Ref. [30] claim, measurements of the weak charges of heavy nuclei (using atomic parity violation experiments) show an experimental constrain on β, typically $\beta < 10^{30}$. This bound can be obtained looking for some β such that $Q_I = Q_{\rm exp}$, where $Q_{\rm exp}$ is the experimental measured value of the weak charge.

The effects of atomic parity violation can be measured either by observing the rotation of the polarization plane of linearly polarized light, or by measuring the rate for a Stark induced transition. The most precise measurement of the weak charge has been performed on a Cesium atom by the Boulder group [31], being $Q^{Cs}_W(\exp) = -72.69 \pm 0.48$ (having into account the combined experimental and theoretical uncertainty about 0.6%). Although experimental work on a chain of rare earth isotopes and cooled and trapped atoms is in progress (see [32] for a recent review), it is doubtful that more restrictive bounds on β can be derived following this approach.

However, the general strategy employed to test P-odd contact effects in gravitation can be employed to estimate, from Eq. (10), bounds on α_2 using inconclusive searches of PVED in chiral molecules. The idea is to put a limit on α_2 by equating the magnitude of the most recent experimental bound on PVED with the corresponding magnitude of a similar effect due to P-odd long-range gravitational effects. To this end, we will review very briefly at the beginning of the next section the order of magnitude expected for the PVED, and finally we will estimate new bounds on α_2. For the sake of completeness, we will also include some comments on the β parameter that appears in contact with P-odd gravity.

III. NEW BOUNDS ON α_2 USING MOLECULAR SPECTROSCOPY

One of the first approaches that have been considered in the past towards an experimental detection of molecular parity violation is based in the resolution of the tiny energy splitting of the electronic spectral lines of opposite enantiomers. Let us recall that if we only consider P-conserving interactions to describe the intramolecular dynamics, the two spectra corresponding to different enantiomers are indistinguishable. If we take into account P-odd terms in the molecular Hamiltonian we obtain, following Eq. (6) and averaging over states corresponding to two opposite enantiomers, $E_L = \langle\Psi_L|V^{\rm PV}_{N-e}|\Psi_L\rangle = -E_R = \langle\Psi_R|V^{PV}_{N-e}|\Psi_R\rangle$, where $\Psi_{L,R}$ is the wave function representing the left (L) or right (R)-handed molecule (let us note that the opposite sign between the energies of the enantiomers, E_L and E_R, is due to the pseudoscalar character of V^{PV}_{N-e}). The important point is to note that any pseudoscalar interaction leads to an energy splitting of the electronic lines of opposite enantiomers, given by $\Delta E^{PV} = |E_L - E_R| = 2E_L = 2E_R$. Up to date, because these PVED are extremely small, they have not been unambiguously detected. Following [33], we can estimate their order of magnitude.

In a nonrelativistic approximation the molecular wave function may always be chosen to be real, while the coordinate part of the potential of Eq. (6) is pure imaginary. So, in order to get a nonzero value one has to invoke the spin-orbit coupling to give a first order correction of the wave function. It is possible to make a rough calculation of the order of magnitude of the PVED based upon dimensional considerations. We know that the matrix element of Eq. (6) between s and p states (only those which have chirality different from zero at the origin) [34] is of the order of $G_F Z^3 \alpha$, while from atomic theory we know that the ratio of the spin-orbit matrix element to the excitation energy is roughly $Z^2\alpha^2$, α being the fine structure constant and Z corresponding to the heaviest element of the molecule. Thus, we obtain $\Delta E^{PV}_{N-e} = G_F \alpha^3 Z^5 \sim 10^{-19} Z^5$ (eV).

There have been several approaches considered to detect molecular parity violation, but so far real experimental efforts have concentrated on measuring PVED using high resolution spectroscopy (for a very complete review see the work by Quack, Stohner, and Willeke [20] and references therein). One of the most promising candidates to detect molecular parity violation is bromochlorofluoromethane (CHFClBr). The energies of different enantiomers of CHFClBr have been compared within a resolution of 10^{-14} eV, with no signal of P violation being observed [21].

We would like to note that chiral molecules are sensitive to any kind of pseudoscalar interaction, in particular, to a possible P-odd gravitational potential. So, it seems difficult to distinguish experimentally between energy splittings due to electron-nucleon interaction and those due to some gravitational P-odd effect. We propose here to interpret bounds on parity violation from atomic and molecular physics experiments in terms of bounds on parity violation in gravitation. In order to do this, we will estimate the energy splitting of the electronic spectra of opposite chiral molecules, assuming that this is due to the P-odd gravitational interaction between the electrons of a chiral molecule and the Earth. In this situation we have, from Eq. (10):

$$\Delta E^{PV}_{\alpha_2} = \alpha_2 \frac{GM}{R^2 c^2 m_e} \sum_i \chi(x_i) \sim \alpha_2 \frac{GMN_e}{R^2 c^2 m_e} \langle \vec{s}_e \cdot \vec{p}_e \rangle \sim \alpha_2 \frac{GMN_e}{R^2 c^2} \langle \hbar v_e \rangle \sim 10^{-31} N_e \alpha_2 v_e \text{ (eV)}, \qquad (12)$$

where M and R are, respectively, the mass and radius of the Earth (we have included $\hbar$ and c to obtain easily some numerical estimations). As we noted before, the tightest experimental bound on PVED in chiral molecules is $\Delta E^{PV}_{N-e} < 10^{-14}$ eV. As this splitting could be due to the Leitner-Okubo-Hari Dass's potential, we conclude

$$\Delta E^{PV}_{\alpha_2} < 10^{-14} \to 10^{-31} N_e \alpha_2 v_e < 10^{-14}. \qquad (13)$$

This formula gives in a simple way a bound on α_2 (a similar procedure was employed by Hari Dass to estimate the electron energy splitting due to the α_1 term [6]). Taking a crude estimation of the molecular electron velocity, for example $v_e \sim 10^{-2}$ c, we get

$$|\alpha_2| < 10^{19} N_e^{-1}. \qquad (14)$$

As was pointed out in the introduction, there is a context dependent relation between the constants that parametrize the potential in Eqs. (1) and (2), such that $\alpha_2 < 10^{19} N_e^{-1}$ corresponds to $A_2 < 10^{-2} N_e^{-1}$. However, as our purpose is to compare the bounds obtained from our method with values previously reported, we will include also some estimations of A_2.

As the experimental bound for ΔE^{PV}_{N-e} was found for CHFClBr, for this molecule we have to consider $N_e \sim 10^2$ electrons. In this case, we get $A_2 < 10^{-4}$. Although this is not, by far, the most stringent bound on A_2, this is, to the best of our knowledge, the first bound on long-range P-odd effects in gravitation reported using quantum mechanical laboratory experiments with chiral molecules. In addition, and most importantly, we obtain $\alpha_2 < 10^{17}$, which improves by some orders of magnitude the bound on α_2 obtained in the past using astrophysical measurements (see Table I). Let us note that, unfortunately, it is doubtful that this approach can lead to more tight results than these. In spite of this, if any parity violating effect (in particular the PVED) is found increasing the experimental sensitivity in the future, we could continue improving this bound.

Let us mention briefly how this approach works with regard to the potential shown in Eq. (3), V^{PV}, and to β in P-odd contact gravity. Concerning the A_v term, if we consider the interaction between the Earth and a polarized electron of a chiral molecule, and taking $\lambda \sim 1$ UA (as in [17]), we obtain $A_v/\hbar c < 10^{-6}$. This bound is not comparable at all with the one obtained by Heckel *et al.*, mainly

TABLE I. Upper bounds on the α_2 parameter. Bounds on A_2 have been included for the sake of completeness although they are context dependent. Let us note that the neutron interference experiment, proposed in Ref. [7], has not been performed. Bounds from Refs. [12–14] have been estimated from astrophysical measurements and those obtained from experiments with trapped atoms have been taken from Ref. [15].

Reference	α_2 upper bound	A_2 upper bound
[7]	10^{13}	10^{-10}
[12]	10^{30}	10^{-3}
[13]	10^{22}	10^{-11}
[14]	10^{21}	10^{-12}
[15]	10^{11}	10^{-22}
This work	10^{17}	10^{-4}

because we are considering interactions between the Earth and only one electron, in contrast with the macroscopic sample used by the authors of Ref. [17]. However, one can speculate about the possibility of using a macroscopic sample of chiral molecules to enhance and to test these and other P-odd effects at quantum mechanical level. Regarding the β parameter, if we take again the tightest bound on PVED for CHFClBr considering $Z = 35$ and $N = 45$ (which corresponds to Br, the heaviest element of the studied molecule), we obtain $\beta < 10^{16}$. Let us note that, although this limit is 14 times more stringent than that which has been obtained using atomic physics experiments, it is still far from being useful to discriminate between P-odd or P-conserving gravity.

IV. CONCLUSION

In this work we have proposed that inconclusive searches of PVED in chiral molecules could provide indirect bounds on the α_2 (or A_2) constant that parametrizes the strength of possible long-range P-odd effects in gravitation. These gravitational P-odd effects are of extraordinary importance because they break the equivalence principle, leading to a failure of general relativity. We have based our estimations on the similarities between Leitner-Okubo-Hari Dass's potential and the parity violating one usually considered when electroweak terms are included in molecular physics calculations. The appearance of the pseudoscalar electron chirality operator in Eqs. (9) and (10) has lead us to conclude that, up to date, the highest experimental sensitivity reached in laboratory searches of PVED implies $\alpha_2 < 10^{17}$. This is, to the best of our knowledge, the first bound of α_2 obtained from quantum mechanical experiments using chiral molecules. In addition, the idea of interpreting bounds on parity violation from atomic and molecular physics experiments in terms of bounds on parity violation in gravitation, allows to improve the previously existing bound on β, an important parameter that appears in some fundamental models which include P-odd effects in general relativity.

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PAPER

Stabilization of chiral molecules by decoherence and environment interactions in the gas phase

Isabel Gonzalo*[a] and Pedro Bargueño[b]

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We study the tunnel dynamics of a chiral molecule between its left (L) and right (R) conformations, under the global effect of collisional decoherence together with the effect of a mean-field generated by the environment where an energetic difference, K, between homochiral and heterochiral interactions is assumed. We show that this decoherence leads unavoidably to equal populations of the L and R chiral conformations even for a high enough value of K which tends to keep localized an initial chiral state. However, we also show that K contributes to the stabilization of an initial L or R state for times that could be many orders of magnitude larger than the tunneling time, in the case the decoherence rate is much greater than the tunneling rate. In this case, an estimation of this stabilization time and a critical tunneling time is made. Even in the case in which the tunneling rate is greater than the decoherence rate, the effect of K is to keep localized the initial chiral state for times greater than the tunneling time. A possible slight chiral asymmetry is also considered.

1 Introduction

The interaction of a chiral molecule with its environment is considered the origin of the loss of coherence of the well defined parity state (superposition of chiral enantiomer states) and also the origin of the stabilization of the localized chiral states. It was Hund[1] who first studied chiral stability *versus* tunneling in a double well potential. In the framework of the Hund model, it was found that, if the collision frequency in a gas of chiral molecules is high enough compared with the tunneling frequency between its chiral left (L) and right (R) conformations, tunneling coherence is quickly lost while the evolution to reach equal populations of $|L\rangle$ and $|R\rangle$ states of an initial chiral sample can become noticeably slow.[2–6] Recently, Trost and Hornberger[7] have identified, using molecular scattering theory, the dominant collisional decoherence mechanism which serves to explain the stabilization of chiral molecules due to a background gas.

The role of molecular interactions in the localization and stabilization of molecular chiral states *versus* superposition states has also been studied by several authors.[8–12] Of particular interest is the work of Jona-Lasinio *et al.*,[13] in which dipole–dipole interactions in pyramidal molecules are considered by means of a mean-field approximation which gives place to a nonlinear eigenvalue equation. This approach explains the localization of the states in pyramidal conformations *versus* delocalized (superposition) ones, and also reproduces spectroscopic experimental results. However, this procedure is not always applicable to all chiral molecules where the dipole moment could not change in sign under the inversion by tunneling. Vardi[14] considered in a simple and ingenious manner a mean-field approximation to account for molecular interactions in a sample of chiral molecules, obtaining a pair of nonlinear coupled equations, the nonlinearity due to the difference between homochiral and heterochiral interactions. When this difference is large enough, the population becomes self-trapped in one of the chiral states, $|L\rangle$ or $|R\rangle$. We note that in these two last approaches, the "dephasing" induced by collisions is not considered.

Finally, let us mention the attempt to explain chiral stability by means of parity violating weak interactions. These interactions would induce a slight asymmetry in the double well, favoring the stabilization of one of the enantiomers with respect to the other one. In this case and for a large enough tunneling time, the chiral states $|L\rangle$ and $|R\rangle$ become in fact eigenstates of the Hamiltonian. However, the predicted parity violating energy difference between the two enantiomers of a chiral molecule, which is of the order of 10^{-13}–10^{-20} eV,[15] has not yet been experimentally proven in spite of the numerous proposals to detect it (see for example ref. 15–22 and references therein). We must also note that its extremely tiny value seems to be not so decisive in the stabilization of localized chiral states in molecules which are not in the ultracold regime.

In this work we deal with a gas of chiral molecules where we consider for each molecule: (i) an energetic difference, K, between homochiral and heterochiral interactions in a

[a] *Departamento de Óptica, Universidad Complutense de Madrid, 28040 Madrid, Spain. E-mail: igonzalo@fis.ucm.es*
[b] *Departamento de Física de Materiales, Universidad Complutense de Madrid, 28040 Madrid, Spain*

mean-field approximation following the work of Vardi,[14] and (ii) decoherence in the superposition state, due to the "dephasing" induced by collisions. We study the global effect of all these contributions as well as the relative effects of each one of them, using a two-state model where $|L\rangle$ and $|R\rangle$ states can be connected only by tunneling. We shall also consider the effect of adding a slight asymmetry in the double well due to a possible chiral influence. The model used and the assumptions made (see next section) are valid for the case of a gas and, in principle, cannot be applied to the condensed phase. We found that, for an initial chiral state ($|L\rangle$ or $|R\rangle$), decoherence induced by collisions leads unavoidably to a racemic mixture of equal populations for L and R enantiomers, although at very long times in some cases. In a certain aspect, this is a different result from that found by Vardi[14] and Jona-Lasinio *et al.*,[13] since, as was previously said, they do not consider such a decoherence phenomenon. However, it does not contradict the result of Jona-Lasino *et al.* concerning the induction of pyramidal localization states in NH_3 and ND_3 molecules on increasing the gas pressure. We analyze both cases, when the collisional decoherence rate is much greater than tunneling rate, and when is lower than or is of the order of tunneling. In both cases the effect of a high enough K is to keep localized an initial chiral state for times greater than the tunneling time.

2 The model and results

In the framework of the double well model, we assume a two-state model for a chiral molecule with two possible chiral states, $|L\rangle$ and $|R\rangle$. If there are no asymmetries in the double well and the molecule is isolated, these chiral states are isoenergetic with energy E_0. These states are connected to each other by tunneling through the double well barrier, so that if H is the Hamiltonian of the molecule, and following a common criterion for signs, we have $\langle L|H|R\rangle = -\delta$, with $\delta > 0$. The energetic splitting between the odd and even eigenstates (superpositions of $|L\rangle$ and $|R\rangle$ states) is then 2δ. A molecular state can be expressed as

$$|\psi(t)\rangle = a_L(t)|L\rangle + a_R(t)|R\rangle. \tag{1}$$

Let us consider the intermolecular interactions proposed by Vardi,[14] introduced by means of a Hartree–Fock technique considering each molecule subjected to a mean-field resulting from all the other molecules. This field has homochiral and heterochiral contributions. For a molecule, the total Hamiltonian in the basis $\{|L\rangle,|R\rangle\}$ reads

$$H = \begin{pmatrix} H_{LL} & -\delta \\ -\delta & H_{RR} \end{pmatrix} \tag{2}$$

with

$$H_{LL} = E_0 + \varepsilon + U_{hom}|a_L|^2 + U_{het}|a_R|^2 \tag{3}$$

$$H_{RR} = E_0 - \varepsilon + U_{hom}|a_R|^2 + U_{het}|a_L|^2 \tag{4}$$

where U_{hom} and U_{het} are interaction strengths due to the homochiral (L–L, R–R) and heterochiral (L–R) interactions with the surrounding molecules, respectively.[14] We have also included a small energy, ε, due to a possible chiral influence.

We use the density matrix formalism to study the temporal evolution of the molecular state submitted to the above Hamiltonian H and to collisional effects of the environment molecules. Since we are interested only in the dynamics of our two-state molecular system, we use the master equation for the *reduced* density matrix of our molecular system. This equation is the result of tracing out the bath degrees of freedom from the equation of motion for the full density matrix of the whole system, molecule and bath. A weak enough coupling molecule-environment (as in a gas) and Markov approximation are assumed. The equation to solve is then

$$\frac{d\rho_{ij}}{dt} = -\frac{i}{\hbar}[H,\rho]_{ij} - \gamma_{ij}\rho_{ij}, \tag{5}$$

with $i,j = L,R$, and decay rates γ_{ij} introduced phenomenologically.

We assume that the temperature of the sample is small enough so that the kinetic energy transferred in the collisions is sufficiently small compared to the barrier separating the chiral states $|L\rangle$ and $|R\rangle$, which can be then connected to each other only by tunneling. This assumption occurs in most cases of interest, even at ambiance temperature. We also assume thermal equilibrium in the sense that there is no net change of population levels due to collisions. In addition we consider the energies δ, ε and the difference $K \equiv U_{het} - U_{hom}$ smaller enough than the rotational levels. We then assume a two-state approach where $\rho_{LL} + \rho_{RR} = 1$.

Denoting by $D \equiv \rho_{LL} - \rho_{RR}$ the population difference between $|L\rangle$ and $|R\rangle$ states, we obtain from the master eqn (5),

$$\frac{d\rho_{LR}}{dt} = -\frac{i}{\hbar}(\delta D - 2\varepsilon\rho_{LR} - KD\rho_{LR}) - \gamma\rho_{LR} \tag{6}$$

$$\frac{dD}{dt} = -\frac{i}{\hbar}2\delta(\rho_{LR} - \rho^*_{LR}), \tag{7}$$

where γ is introduced phenomenologically to account for the decay of coherence due to the "dephasing" induced by collisions (the most frequent ones are elastic collisions). This decay is usually expressed as $\gamma = 1/T_2$ where the so-called "transversal" time, T_2, is here of the order of the average time between collisions. Since the eventual ε is assumed to be smaller enough than the thermal energy kT, we can neglect the thermal equilibrium population difference, D_{eq}, to which D relaxes in eqn (7). We note the nonlinear term dependent on K in eqn (6). If this term is zero ($K = 0$), the above equations reduce essentially to those studied by several authors,[2–7] some of them performed a detailed treatment of collisions.[3,6,7] For $\gamma = 0$ and $\varepsilon = 0$ the solution of the equations was studied by Vardi,[14] for different values of K/δ and different initial conditions of $|\psi(t)\rangle$. He showed that, when the nonlinearity is sufficiently large, the population is trapped in one of the wells of the symmetric double well potential. However, in our case it is easy to see that the stationary solution of eqn (6) is

$$\rho^{st}_{LR} = \frac{\delta D}{KD + 2\varepsilon + i\hbar\gamma}, \tag{8}$$

which together with the stationary condition of eqn (7), (ρ^{st}_{LR} real), leads from eqn (8) to the stationary solution $\rho^{st}_{LR} = 0$ and then to $D^{st} = 0$. Thus, in the stationary state, the loss of coherence impedes the existence of superposition states, $|L\rangle$ and $|R\rangle$ states, and a mixed state is then obtained. Since the populations for $|L\rangle$ and $|R\rangle$ states become equal, we get an ensemble of molecules where 50% of them are the L enantiomer and 50% are the R enantiomer, *i.e.*, we have a racemic mixture. This fact was called "racemization by dephasing" by Silbey and Harris.[6] As we see, the decoherence due to γ leads unavoidably to racemization whatever the value of K, in contrast to the result of Vardi in which such a decoherence phenomenon was not considered. For an initial pure chiral sample, the random collisions induce dephasing not only in the tunneling dynamics of each molecule interrupting its coherent tunneling, but also induce dephasing between the tunnel dynamics of different molecules. This last mechanism tends to equal the populations of $|L\rangle$ and $|R\rangle$ states, despite the tendency of the population to be trapped in one of the wells by the mean-field effect governed by K.

We study the solutions of eqn (6) and (7) in two different cases: $\gamma \gg \delta/\hbar$ and $\gamma \lesssim \delta/\hbar$.

• *Case* $\gamma \gg \delta/\hbar$. Let us first consider the usual case in which the average time between collisions is much smaller than the tunneling time, $t_\delta = \hbar/\delta$, of the isolated molecule, *i.e.*, the decoherence process governed by γ is much faster than tunneling. In this case we can consider that eqn (6) evolves much faster than eqn (7), the population difference D being scarcely changed while the coherence ρ_{LR} reaches the stationary state given by eqn (8). Hence, by inserting eqn (8) in (7) and taking into account that the initial condition of $D(t)$ is D_0, we easily obtain

$$t = \frac{K^2}{8\delta^2\gamma}(D_0^2 - D^2) + \frac{K\varepsilon}{\delta^2\gamma}(D_0 - D) + \left(\frac{\varepsilon^2}{\delta^2\gamma} + \frac{\gamma\hbar^2}{4\delta^2}\right)\ln\frac{D_0}{D}. \tag{9}$$

We define the time t_r as the time necessary for the population difference D diminishing from the initial value D_0 to the value D_0/e. It characterizes the stabilization time of an initial chiral state and is of the order of the racemization time since the coherence is completely lost when $D = 0$, as shown in eqn (8). This time can be appreciated in the decay curves $D(t)$ of Fig. 1 and 2, commented below. The time t_r can be obtained from the preceding equation, and reads

$$t_r = \left(1 - \frac{1}{e^2}\right)\frac{K^2D_0^2}{8\delta^2\gamma} + \left(1 - \frac{1}{e}\right)\frac{KD_0\varepsilon}{\delta^2\gamma} + \frac{\varepsilon^2}{\delta^2\gamma} + \frac{\gamma t_\delta^2}{4}, \tag{10}$$

where the contributions of the different physical phenomena are displayed. We note that the terms dependent on K or ε decrease

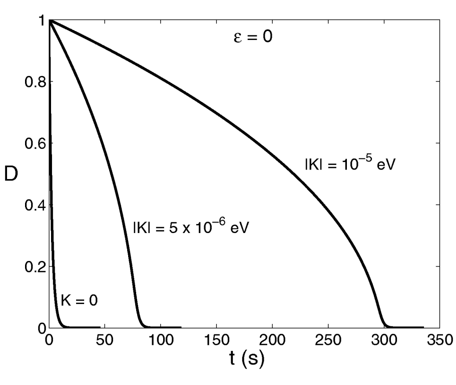

Fig. 1 Population difference $D(t) \equiv \rho_{LL}(t) - \rho_{RR}(t)$ as a function of time, for $t_\delta = 10^{-4}$ s, $\gamma = 10^9$ s^{-1}, in the case $\varepsilon = 0$, and values: $K = 0$, $|K| = 5 \times 10^{-6}$ eV, $|K| = 10^{-5}$ eV.

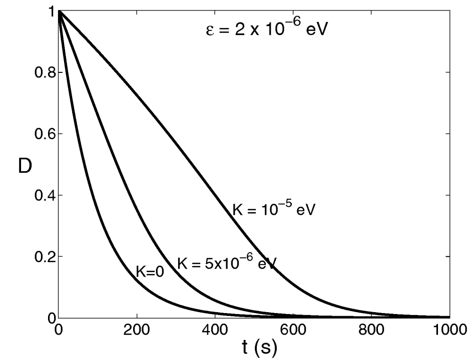

Fig. 2 Population difference $D(t) \equiv \rho_{LL}(t) - \rho_{RR}(t)$ as a function of time, for $t_\delta = 10^{-4}$ s, $\gamma = 10^9$ s^{-1}, in the case $\varepsilon = 2 \times 10^{-6}$ eV, and values: $K = 0$, $K = 5 \times 10^{-6}$ eV, $K = 10^{-5}$ eV.

when γ increases, while the opposite behaviour occurs in the known last term.[7] The terms proportional to K^2 or ε^2 contribute to augment the time t_r whatever the sign of K or ε. All the terms are inversely proportional to δ^2, *i.e.*, we have a parabolic behavior, $t_r \propto t_\delta^2$, which allows us to easily define a critical tunneling time t_c at which $t_r = t_\delta$. It is given by

$$t_c = \left[\left(1 - \frac{1}{e^2}\right)\frac{K^2D_0^2}{8\hbar^2\gamma} + \left(1 - \frac{1}{e}\right)\frac{KD_0\varepsilon}{\hbar^2\gamma} + \frac{\varepsilon^2}{\hbar^2\gamma} + \frac{\gamma}{4}\right]^{-1}. \tag{11}$$

Then, for $t_\delta < t_c$, we obtain $t_r < t_\delta$, while for $t_\delta > t_c$, we obtain $t_r > t_\delta$.

In order to better analyze and estimate t_r, let us consider the case in which $\varepsilon = 0$. In this case t_r is reduced to

$$t_r = t_K + t_\gamma, \tag{12}$$

where we define $t_K \equiv (1 - \frac{1}{e^2})\frac{K^2D_0^2}{8\delta^2\gamma}$ and $t_\gamma \equiv \frac{\gamma t_\delta^2}{4}$ from eqn (10). We must note that under the condition $\gamma \gg t_\delta^{-1}$ we are assuming t_γ is always greater than t_δ, as can be easily seen. We can define a critical tunneling time, t_{Kc}, at which $t_K = t_\delta$. It is given by

$$t_{Kc} = \left[\left(1 - \frac{1}{e^2}\right)\frac{K^2D_0^2}{8\hbar^2\gamma}\right]^{-1}. \tag{13}$$

Then, for $t_\delta > t_{Kc}$, the contribution of t_K to the time t_r is greater than the tunneling time t_δ. It is also easy to see that for $D_0 = 1$ and $K \gtrsim 1.53\hbar\gamma$, we obtain $t_K > t_\gamma$. Table 1 shows, for $D_0 = 1$ (initial chiral purity), the order of magnitude of the values of t_γ and t_K, for different values of t_δ, γ (with $\gamma \gg t_\delta^{-1}$) and K. The decay rate γ, related to the frequency of elastic collisions, could be assumed to be of the order of 10^{11}–10^{12} s^{-1} for a gas at normal conditions, and of the order of 10^8 s^{-1} for a gas at very low pressure and ambiance temperature. The value of K can be expected to be comprised in a large range of values, depending, among others, on the density of the gas.[23] Here we take values of K of the order of 10^{-5}–10^{-6} eV. With respect to δ, it is known that there is a large range of possible values.[15]

Only for the values displayed in the first row of the table, t_K results lower than t_δ, corresponding to a case in which $t_\delta < t_{Kc}$. For the rest of the values, the most remarkable result is that, for a large range of values, the times t_γ and t_K are many orders of magnitude greater than t_δ, leading to an almost complete

Table 1 Several values of $t_\delta \equiv \hbar/\delta$, γ (with $\gamma \gg t_\delta^{-1}$) and K, from which the orders of magnitude of t_γ and t_K are obtained for $D_0 = 1$. The time t_r for $\varepsilon = 0$ is $t_r = t_\gamma + t_K$

t_δ (s)	γ (s^{-1})	K (eV)	t_γ (s)	t_K (s)
10^{-9}	10^{12}	10^{-5}	10^{-7}	10^{-11}
10^{-4}	10^{9}	10^{-5}	1	10^{2}
10^{-3}	10^{8}	10^{-6}	10	10^{3}
10^{-3}	10^{11}	10^{-5}	10^{4}	10^{2}
1	10^{8}	10^{-6}	10^{7}	10^{9}
1	10^{11}	10^{-5}	10^{10}	10^{8}

stabilization of the initial chiral state. The huge values (10^9, 10^{10} s) of the time t_r in cases with $t_\delta \sim 1$ s are noticeable.

The terms dependent on ε in eqn (10) contribute to t_r in a very similar way as the evaluated term t_K does when $D_0 = 1$. If ε is the intrinsic parity violating energy, of the order of 10^{-15} eV, its contribution to t_r is evidently negligible compared with t_K and t_γ. However, other chiral influences coming from external fields could be considered.

The solution for the population difference $D(t)$ is easily obtained from eqn (9) (valid for $\gamma \gg t_\delta^{-1}$) in the case $K = 0$, and reads $D(t) = D_0 e^{-t/t_\gamma}$ with $t_r = \frac{\varepsilon^2}{\delta^2\gamma} + \frac{\gamma t_\delta^2}{4}$. For $K \neq 0$, the solution $D(t)$ is easily obtained by means of a t–D plot of eqn (9), as is shown in Fig. 1, for the case $\varepsilon = 0$, $t_\delta = 10^{-4}$ s and $\gamma = 10^9$ s^{-1}. In this figure we observe the nonlinear effect of K on the decay of $D(t)$ which is far from an exponential decay and becomes slower than the decay obtained for $K = 0$, the racemization time being of the order of 100 s or more. We recall that the coherence is completely lost when $D = 0$. We note that for $\varepsilon = 0$ the results are independent of the sign of K.

In Fig. 2 we observe the effect of a possible external chiral influence so that $\varepsilon = 2 \times 10^{-6}$ eV, with the same values for the other parameters used in Fig. 1. The increase in the time decay (note that the values on the X-axis are higher than in Fig. 1) is remarkable. If K and ε have different sign, the decay is somewhat faster than in the case they have the same sign, as can be inferred from eqn (10). If ε is greater enough, $D(t)$ tends to exhibit an exponential decay, as expected from inspection of eqn (9).

In all the cases analyzed above, $D(t)$ does not oscillate due to the high enough γ compared with t_δ^{-1}. When the solutions $D(t)$, shown in Fig. 1 and 2, are compared with the exact solutions obtained numerically from eqn (6), (7), it can be seen that if γ is only five times greater than t_δ^{-1}, the approximate solutions differ from the exact ones by less than 0.1 per cent.

• *Case* $\gamma \lesssim \delta/\hbar$. Let us now analyze the case in which γ is of the order of or lower than t_δ^{-1}, which means that the average time between collisions is longer than or of the order of the tunneling time $t_\delta = \hbar/\delta$. In this case, the solution $D(t)$ as well as the coherence $\rho_{LR}(t)$ are obtained numerically from eqn (6), (7), and shown in Fig. 3 for several cases.

First we consider $\varepsilon = 0$ and $\gamma = 0$. For $K/\delta \gtrsim 4$, Vardi[14] found that the population is trapped in the initial chiral state, while for lower values of K/δ, $D(t)$ oscillates around $D = 0$. For the initial condition $\rho_{LL} - \rho_{RR} = 1$, we show in Fig. 3(a) and (b) the case for $K/\delta = 10$, which exhibits the same oscillating

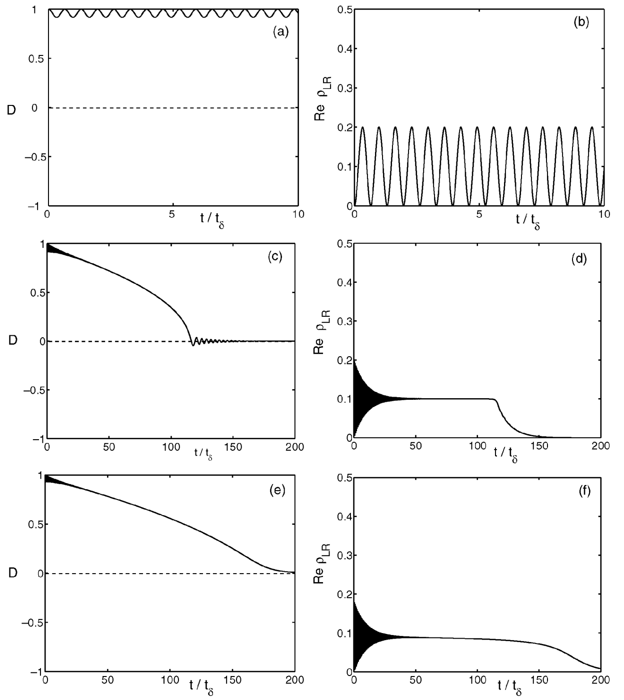

Fig. 3 For $K/\delta = 0$, population difference $D \equiv \rho_{LL}(t) - \rho_{RR}(t)$ and the real part of the coherence ρ_{LR} *versus* the normalized time t/t_δ, in cases (a) and (b): $\gamma = 0$ and $\varepsilon/\delta = 0$; (c) and (d): $\gamma t_\delta = 0.1$ and $\varepsilon/\delta = 0$; (e) and (f): $\gamma t_\delta = 0.1$ and $\varepsilon/\delta = 0.5$. The oscillations of D in (c) and (e), and coherence in (d) and (f), at short times, cannot be resolved at the scale of the figure.

behavior for all times. When the collisional decoherence is introduced, the solutions are of the type obtained for $\gamma t_\delta = 0.1$, shown in Fig. 3(c) and (d). We see that the population difference, D, first decays with small oscillations (scarcely seen in the figure), but without changing the sign of the chirality of the sample. However, for longer times, the regime imposed by γ dominates, leading unavoidably to racemization since $D = 0$ is reached at the same time in which coherence is lost ($\rho_{LR} = 0$). This is obtained in a time longer than tunneling (two orders of magnitude greater than t_δ in this case). Correspondingly, the coherence behaves differently for short times and for long times. For a lower γt_δ value, or (and) a higher K/δ value, the decay is much more slower. For example, for the same values as before except that $K/\delta = 20$, the racemization time results to be three orders of magnitude greater than t_δ. This result is also obtained for the same values as in Fig. 3(c) and (d) except that $\gamma t_\delta = 0.01$. However, the ratio t_r/t_δ is much lower than in the case where $\gamma \gg \delta/\hbar$. Finally, if there is a small chiral influence such that $\varepsilon/\delta = 0.5$ for example, the solutions decay slower than in the cases (c) and (d), as shown in Fig. 3(e), (f).

3 Conclusion

We have studied the temporal evolution of the molecular state of a chiral molecule in which both chiral enantiomers L and R are only connected by tunneling. We have considered a decoherence effect due to the "dephasing" induced by collisions in tunnel dynamics, together with the effect of a mean-field generated by the environment where an energetic difference, K, between homochiral and heterochiral interactions is assumed. A possible slight asymmetry in the double well has also been considered. We have shown that the presence of the mentioned decoherence leads unavoidably to equal populations of $|L\rangle$ and $|R\rangle$ chiral states, even for a high enough value of K which tends to keep localized an initial chiral state. This result is in contrast with the case where this decoherence effect is absent.[13,14]

In the case in which the decoherence rate is much greater than the tunneling rate, it is found that the known stabilization of a chiral state promoted by collisional decoherence could be enhanced and even dominated by the contribution of K, the stabilization time being many orders of magnitude larger than the tunneling time for a wide range of the parameter values. An estimation of this stabilization time is made. A critical tunneling time above which the stabilization time induced by K is longer than tunneling is obtained.

In the case in which the decoherence decay rate is smaller than or of the order of the tunneling rate, the effect of a high enough value of K to stabilize an initial chiral state[14] becomes drastically reduced by the collisional decoherence, but in spite of it, a stabilization of the initial chiral state for times longer than tunneling is obtained. However, these times are not so long as in the preceding case.

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Friction-induced enhancement in the optical activity of interacting chiral molecules

Pedro Bargueño [a,*], Helen C. Peñate-Rodríguez [b,c], Isabel Gonzalo [d], Fernando Sols [a], Salvador Miret-Artés [c]

[a] Departamento de Física de Materiales, Universidad Complutense de Madrid, E-28040, Madrid, Spain
[b] Instituto de Física Fundamental (CSIC), Serrano 123 E-28006, Madrid, Spain
[c] Instituto Superior de Tecnologías y Ciencias Aplicadas, Ave. Salvador Allende y Luaces, Quinta de los Molinos, Plaza, 10600 La Habana, Cuba
[d] Departamento de Óptica, Universidad Complutense de Madrid, E-28040, Madrid, Spain

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ABSTRACT

The stability of chiral molecules described by a non-linear two-state system which accounts for mean–field interactions between different isomers, including any external chiral influence (in particular, the parity violating energy difference) is investigated. By introducing the population and phase difference of the chiral states as a pair of canonical variables, driving an analogy to a bosonic Josephson junction, our study to include dissipative effects in condensed phase described by a Caldeira–Leggett like Hamiltonian is extended using the Langevin formalism. Dissipative effects produce an enhancement in the population difference, not leading to racemization.

1. Introduction

A chiral molecule is usually described by means of a double well potential where one of the minima corresponds to the right-handed, *R*, and the other to the left-handed, *L*, enantiomers, respectively. The high stability of the enantiomers was reported by Hund [1] as a paradox since they are not eigenstates of the parity invariant Hamiltonian of the molecule and was explained by the very long tunneling time (due to high barriers or/and high mass) connecting both conformations. However this does not explain the difficulty to prepare superposition states of definite parity, apart from a possible decoherence process induced by the environment [2]. In addition, the presence of the parity violating electroweak interaction modifies the traditional description of chiral molecules. As was first stated by Lethokov and others [3–5], this interaction predicts a parity violating energy difference (PVED) between the two enantiomers which renders the double well potential slightly asymmetric. In this case, the Hamiltonian for the isolated chiral molecule under the two-state approximation (very low temperatures) in the $\{|L\rangle, |R\rangle\}$ basis becomes

$$\hat{H}_0 = \begin{pmatrix} \epsilon_{\rm PV} & \delta \\ \delta & -\epsilon_{\rm PV} \end{pmatrix}, \qquad (1)$$

where $2\epsilon_{\rm PV}$ is the PVED, and $2\,\delta$ (with $\delta > 0$) is the energy difference between the eigenstates $|1\rangle$, $|2\rangle$, being related to the height of the barrier of the double well potential (δ is inversely proportional to the tunneling time interchanging chiral conformations through the barrier; the two-level system was discussed in relation to the PVED in [6,7]). In the asymmetric case, the eigenstates of $\hat{H}_0$ are related to the eigenstates of definite parity as

$$\begin{pmatrix} |1\rangle \\ |2\rangle \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} |L\rangle \\ |R\rangle \end{pmatrix}, \qquad (2)$$

where the mixing angle, θ, is given by

$$\tan 2\theta = \frac{\delta}{\epsilon_{\rm PV}}. \qquad (3)$$

As a consequence, when $\epsilon_{\rm PV}$ is much larger than δ, i.e., $\delta/\epsilon_{\rm PV} \to 0$, the states $|L\rangle$ and $|R\rangle$ tend to be the eigenstates, apparently solving the "paradox" for the isolated molecule. However, although the weak interaction has been observed in atoms, it has not been observed in molecules yet. In particular, the predicted value of PVED between enantiomers of a chiral molecule between 10^{-18} and 10^{-13} eV [8–13], has not found experimentally in a conclusive manner, although there are some experimental results that could be related to such a difference [14].

Concerning the interaction of chiral molecules with the environment, numerous and different approaches have been developed in order to understand the stability of chiral conformations and the loss of coherence of the superposition states $|1\rangle$ and $|2\rangle$. Apart from the possible naive model of the double well potential, it is well known that the environment induces decoherence and it is a still open question why the environment selects in this process only the chiral states $|L\rangle$, $|R\rangle$ and not $|1\rangle$, $|2\rangle$, as pointed out by Simonius [15] and Harris [2,16]. It was found that if environment interaction times are higher than the tunneling time, the enantiomer (chiral) states are then prevented from tunneling between each other and the superposition of states is rapidly incoherent. A standard relaxation theory was used to relate the damping due to the

* Corresponding author.
E-mail address: p.bargueno@fis.ucm.es (P. Bargueño).

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environment to classical friction, explaining the stability of handedness in terms of the damped oscillator [17]. A variational calculation of the dynamics of a two-level system interacting with a bath was also reported [18,19]. Of particular interest is the work by Jona-Lasinio [20] and coworkers, in which dipole–dipole interactions were shown to induce localization in a gas of pyramidal chiral molecules. Very recently, Trost and Hornberger [21] have used the S-matrix theory of Harris and Stodolsky [16], with an explicit dipole–quadrupole interaction, to examine the rapid decay to equal populations of the parity eigenstates, which partially answers why parity eigenstates are not seen. Racemization (the evolution towards a sample of equal number of L and R isomers) by tunneling was also the subject of several works by Cattani and Bassalo [22,23]. They considered an interaction potential between the chiral and the perturbing molecules, this cooperative interaction was understood as a Hartree field and its effects evaluated in the framework of the time-dependent Schrödinger equation. Then, under the Hartree approximation, and for a molecular state described by

$$|\psi(t)\rangle = a_L(t)|L\rangle + a_R(t)|R\rangle, \tag{4}$$

a pair of linear coupled equations for the chiral amplitudes $a_L(t)$ and $a_R(t)$ were obtained. Subsequent improvements on the description of chiral stability were included by Vardi [24], who employed a Hartree–Fock-type technique to account for the interaction between each molecule and the mean–field (MF) induced by the remaining molecules of the sample, resulting in two coupled non-linear dynamical equations. When the non-linearity (given by the difference between homochiral and heterochiral interactions due to the MF) is sufficiently large, population is surprisingly trapped in one of the wells even if the potential is perfectly symmetric. In addition, in analogy to condensed phase studies, a Caldeira–Leggett Hamiltonian model was also used to simulate the interaction with a bath described by a bilinear system–bath coupling [25].

Let us then recall the approach of Vardi in which each molecule is subject to a MF which has two components, U_{hom} and U_{het}, due to the homochiral (L–L, R–R) and heterochiral (L–R) interactions with the surrounding molecules, respectively (the geometrical difference between enantiomers induces steric effects that cause the interaction potentials for the L–L (or R–R) and L–R pairs of molecules to be different [26–28]).

He found, for a molecular state given by Eq. (4), the following coupled non-linear equations for the chiral amplitudes ($\hbar = 1$):

$$\frac{da_L}{dt} = -i\left(\omega + \kappa|a_R|^2\right)a_L + ia_R$$
$$\frac{da_R}{dt} = -i\left(\omega + \kappa|a_L|^2\right)a_R + ia_L, \tag{5}$$

where $\omega = U_{hom}/\delta$, $\kappa = (U_{het} - U_{hom})/\delta$, and the time has been rescaled as $\omega t \to t$. As pointed out by the same author [24], Eq. (5) have been extensively studied in the context of the Bose–Hubbard Hamiltonian description of the Josephson oscillations between two trapped Bose–Einstein condensates [29,30], exhibiting a rich and complex behavior depending on the non-linear term κ. It is remarkable that, when $\kappa \gg 1$, the population is trapped in one of the wells (this is the analogous of the so-called *macroscopic quantum self trapping* for two weakly coupled condensates).

In this work, the stability of chiral molecules is studied by adding to the two-state model of Vardi [24], the intramolecular weak interaction ϵ_{PV} (or any chiral external influence, ϵ) and bath-induced interactions due to an additional medium by means of a Caldeira–Legget like Hamiltonian in the Langevin formalism for open systems. In this way, previous results by Harris and coworkers are thus recovered and generalized. In addition, quantitative results on the enhancement of the population difference (optical activity) due to dissipation are also provided.

2. A Hamiltonian description of interacting chiral molecules

Let us write the effective Hamiltonian of the two-level system as

$$\hat{H} = \begin{pmatrix} \epsilon + \kappa(|a_L|^2 - |a_R|^2) & \delta \\ \delta & -\epsilon - \kappa(|a_L|^2 - |a_R|^2) \end{pmatrix}; \tag{6}$$

and the wave function for the chiral molecule, Eq. (4), as

$$|\psi\rangle = |a_L(t)|\, e^{i\phi_L(t)}|L\rangle + |a_R(t)|\, e^{i\phi_R(t)}|R\rangle. \tag{7}$$

Then, in terms of the phase difference $\Phi = \phi_L - \phi_R$ and population difference $z = |a_L|^2 - |a_R|^2$, Eq. (5) can be expressed, including an asymmetry between the two wells, ϵ, as

$$\dot{z}(t) \equiv \frac{dz}{dt} = -\sqrt{1-z^2}\sin\Phi$$
$$\dot{\Phi}(t) \equiv \frac{d\Phi}{dt} = -\frac{\kappa}{2\delta}z + \frac{z}{\sqrt{1-z^2}}\cos\Phi - \frac{\epsilon}{\delta}. \tag{8}$$

Thus, Eq. (8) represent the dynamical equations for the chiral population and phase difference for an ensemble of chiral molecules, described by a two-level system which include tunneling and parity violation (or any chiral external influence) and in presence of MF interactions with other molecules of the ensemble. Notice that the asymmetry ϵ can contain in general both the ϵ_{PV} and some possible chiral discriminating energy coming from, for instance, an average interaction with polarized fields. In what follows, the effect of the PVED will not be considered since its energy scale is extremely small compared to that of κ, which is of the order of the van der Waals energies between molecules. The thermodynamic behavior of chiral mixtures is very sensitive to the sign of κ, its different sign giving place to different phase diagrams of theses mixtures. Molecular conglomerates are found when the heterochiral interaction strength is smaller than the homochiral value. Thus, only the case for $\kappa < 0$ will be analyzed here. For the sake of completeness, positive values of κ will be briefly commented.

Furthermore, the z, Φ variables can be seen as canonically conjugate, obeying the Heisenberg equations of motion which are formally identical to the Hamilton equations of motion, $\dot{z} = -i[z, H] = -\frac{\partial H}{\partial \Phi}$, $\dot{\Phi} = -i[\Phi, H] = \frac{\partial H}{\partial z}$, where the (adimensional) Hamiltonian is given by

$$H = \frac{1}{4}\frac{\kappa}{2\delta}z^2 - \sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z. \tag{9}$$

Let us note that in fact $H = \langle\hat{H}\rangle_\psi$ and the dynamics of the sample of interacting chiral molecules here considered can be rationalized in terms of the Hamiltonian of Eq. (9). This Hamiltonian is identical to that used for a non-rigid momentum-shortened pendulum of length $\sqrt{1-z^2}$ which has also used in the context of trapped Bose–Einstein condensates [29,30]. Even more, when $\kappa = 0$, this Hamiltonian can be used to describe an isolated chiral molecule or, more generally, any isolated two-level system. Thus, we could establish the following theorem:

Theorem 1. *Any isolated two-level system can be represented by the Hamiltonian* $H = -\sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\Delta}z$, *where* δ *gives the tunneling coupling,* ϵ *the asymmetry and* z *and* Φ *the population and phase difference of the system, respectively.*

One of the advantages of this Hamiltonian description is that, in general, it makes easier to introduce bath effects through a Caldeira–Leggett like model [31]. Thus, starting from the Hamiltonian of Eq. (9), in the following section the dynamical time dependent equations for z and Φ, including both MF and bath-induced interactions, will be derived.

3. Dissipative dynamics of interacting chiral molecules

Noting that, in Eq. (9), Φ and z play the role of a generalized momentum and coordinate, respectively, one can introduce a system-bath bilinear coupling *via* a Caldeira–Legget like approach leading to the following Hamiltonian:

$$H = \frac{1}{4}\frac{\kappa}{2\delta}z^2 - \sqrt{1-z^2}\cos\Phi + \frac{\epsilon}{\delta}z + \frac{1}{2}\sum_i\left(\frac{\Lambda_i}{2}z_i^2 + \frac{\Phi_i^2}{2\Lambda_i}\right) - \Phi\sum_i c_i\Phi_i + \Phi^2\sum_i\frac{c_i^2}{2}\Lambda_i, \quad (10)$$

where the sums run over the bath oscillator coordinates $\{z_i, \Phi_i\}$ and Λ_i and c_i are suitable dimensionless constants representing generalized masses and couplings with the environment, respectively. The great advantage of this model relies on the fact that the environmental degrees of freedom can be eliminated exactly from the equations of motion. It should be stressed at this point that the main difference between this Caldeira–Leggett coupling and other models previously used [17–19] is the potential renormalization introduced by the term which goes with the square of the generalized position.

After eliminating the environmental degrees of freedom using the Langevin formalism [32,33], Hamilton's equations of motion for $z(t)$ and $\Phi(t)$ read now as

$$\dot{z} = -\sqrt{1-z^2}\sin\Phi - \int_0^t \gamma(t-s)\dot{\Phi}(s)ds - \xi(t)$$
$$\dot{\Phi} = -\frac{\kappa}{2\delta}z + \frac{z}{\sqrt{1-z^2}}\cos\Phi - \frac{\epsilon}{\delta}, \quad (11)$$

where

$$\gamma(t) = \sum_i \Lambda_i c_i^2 \cos t, \quad (12)$$

is the damping kernel and the driving force

$$\xi(t) = \sum_i (c_i(\Phi_i(0) - c_i\Lambda_i\Phi(0))\cos t + z_i(0)\Lambda_i \sin t), \quad (13)$$

represents a stochastic force, depending on the initial conditions of both the dynamical system and the bath. In a classical regime, if these initial conditions are zero, the stochastic force vanishes leading to a pure dissipative dynamics and no contribution coming from the zero point motions of bath oscillators are present. This situation is usually considered at high temperatures where the classical noise is assumed to be a gaussian white process with zero mean and autocorrelation function described by a Dirac delta function. However, in our context, the temperature has to be very low in order to stay within the two-level system framework and, therefore, quantum noise should be taken into account in the tunneling dynamics. In quantum dissipation, the dynamics cannot be strictly invariant under translations and it is related to the choice of initial conditions. This problem was studied and solved by introducing the so-called Fröhlich type Hamiltonians [34]. Even more, the noise autocorrelation function is complex and the corresponding stochastic process is neither gaussian nor white, although it is of zero mean when averaged over the bath. In contrast to the classical case, such correlation decays algebraically [32,33] as t^{-2}.

All quantities characterizing the environment may be expressed in terms of the spectral density of the bath oscillators, $J(\omega)$. The most frequently used spectral density, $J(\omega) = \frac{2\delta}{\kappa}\gamma\omega$, is associated with the so-called Ohmic damping. For this case, the damping kernel reads [33] $\gamma(t) = 2\gamma\delta(t)$, which renders Eq. (11) memory free, recovering the velocity proportional damping term familiar from classical damped systems. Thus, the coupled dynamical equations in the MF approximation, with bath-induced interactions (Ohmic friction) and averaged on the bath oscillators are finally given by

$$\dot{z} = -\sqrt{1-z^2}\sin\Phi - \gamma\dot{\Phi}$$
$$\dot{\Phi} = -\frac{\kappa}{2\delta}z + \frac{z}{\sqrt{1-z^2}}\cos\Phi - \frac{\epsilon}{\delta}. \quad (14)$$

where the bath averages over the physical variables $\langle z\rangle$ and $\langle\Phi\rangle$ have been again denoted by z and Φ in order to use a simplified notation from now on. These two non-linear and coupled dynamical equations have to be solved with a previous stability analysis in terms of four parameters (κ, δ, ϵ and γ) to provide a complete and satisfactory understanding of this dynamical system (see Appendix). In other words, it is expected that for several sets of parameters describing tunneling, MF interactions, chiral and dissipative effects, a localization in one of the wells or a racemization of the sample can take place.

4. Results

Before carrying out a systematic numerical analysis of the solutions of the damped system described by Eq. (14) and its physical consequences, it is interesting to consider first the non-interacting case. In absence of damping, the population difference can be expressed in terms of quadratures as

$$t_0 - t = \int_{z(0)}^{z(t)} \frac{dz}{\sqrt{P(z)}}, \quad (15)$$

where

$$P(z) = \sqrt{\frac{1}{16}A^2z^4 + 2ABz^3 + Cz^2 + 2H_0Bz + 1 - H_0^2}, \quad (16)$$

with $A = \kappa/2\delta$, $B = \epsilon/\delta$, $C = 2H_0A - B^2 - 1$ and H_0 the conserved energy. If $\kappa = 0$ and $\Phi(0) = 0$,

$$z(t) = z(0)\frac{\epsilon^2 + \delta^2\cos(2\sqrt{\delta^2+\epsilon^2}t)}{\delta^2+\epsilon^2}, \quad (17)$$

the time average being

$$\langle z(t)\rangle = z(0)\frac{1}{1+(\frac{\delta}{\epsilon})^2}. \quad (18)$$

as previously reported by Harris and Stodolsky [2] by replacing ϵ by ϵ_{PV}. Notice that, in general, this time average value is greater than the amplitude of the oscillations of $z(t)$. In addition, if $B = 0$ (symmetric configuration), the well known symmetric tunneling oscillations are also recovered.

The stationary points for the bath average values (z,Φ) of Eq. (14) obtained from the conditions $\dot{z}(t) = 0$ and $\dot{\Phi}(t) = 0$ are $(0, n\pi)$ and $(\pm\sqrt{1-A^{-2}}, n\pi)$ where $A = \kappa/2\delta$ (see Appendix). These stationary points are also the same for the undamped system ($\gamma = 0$), Eq. (8), and for the symmetric configuration ($\epsilon = 0$). Only the case with $n = 0$ will be analyzed in order to simplify the physical discussion. Finally, the initial condition for the phase will be always the same, $\Phi(0) = 0$, and κ and ϵ will be given in units of δ.

In absence of dissipation and chiral effects, the time evolution of the population difference issued from solving Eq. (8) is plotted in Figure 1. When $z(0) \sim 1$, the reported self-trapping result by Vardi [24] is reproduced by changing $|\kappa|$, or the MF interaction, from $\kappa = -2$ (black curve) to $\kappa = -5$ (blue curve). The population is trapped in one of the two chiral states for a symmetric double well configuration. We point out that $\kappa = -2$ corresponds to the non-interacting regime and thus the oscillations are due to the tunneling process. On the contrary, for $\kappa = -5$ the dynamics is mainly driven by the MF interactions.

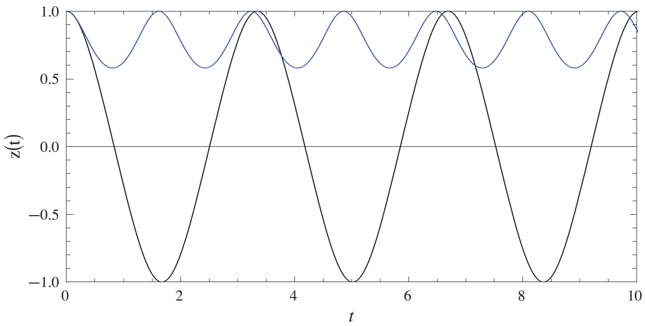

Figure 1. Oscillating population difference versus time for the initial conditions z(0) ∼ 1 and $\Phi(0) = 0$ with $\epsilon = \gamma = 0$. The effect of the MF interaction on the localization is shown by changing κ from $\kappa = -2$ (black) to $\kappa = -5$ (blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

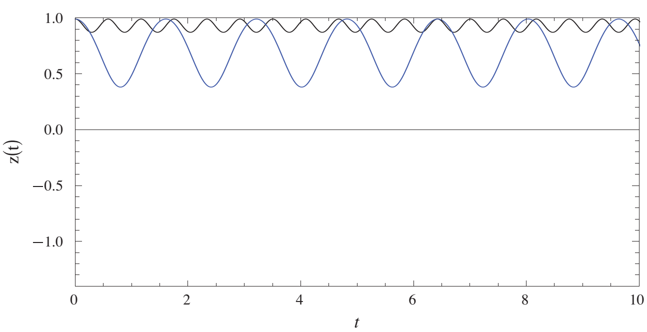

Figure 2. Oscillating population difference versus time for the initial condition $z(0) \sim 1$, with $\gamma = 0$ and $\kappa = -5$ (in units of δ) for two different values of ϵ: $\epsilon = 3$ (blue curve) and -3 (black curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

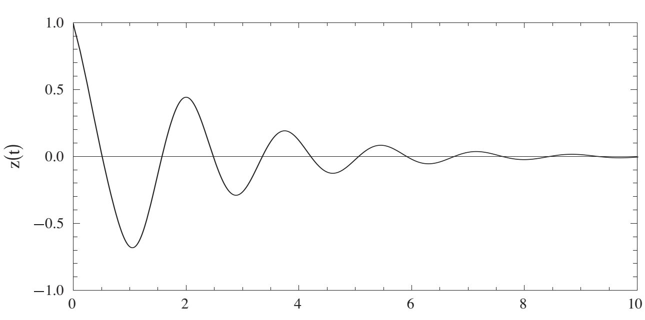

Figure 3. Population difference versus time in presence of damping $\gamma = 0.07$ and $\kappa = -5$ and $\epsilon = 0$ The initial condition is $z(0) \sim 1$.

A quite different behavior is observed in Figure 2 when a non-zero chiral external influence, $\epsilon \neq 0$, of the order of magnitude of κ is present. A higher localization is reached when ϵ and κ have the same sign. This behavior can be easily understood by noting the sign of the first and third term in Eq. (14) for $d\Phi/dt$. On the contrary, when they have opposite sign, their effects are compensated. The stationary points in these cases are unstable since they are saddle points (see Appendix).

In order to investigate the effect of dissipation in the time evolution of this dynamical system, several cases can be considered. In Figure 3 it is plotted the population difference for the initial condition $z(0) \sim 1$ when $\gamma = 0.07$, $\kappa = -5$ and $\epsilon = 0$. The racemization is rapidly achieved after four oscillations. As mentioned in the Appendix, the stability around this stationary point is asymptotic. If the effect of an external chiral influence is included with the same initial condition for z, the observed behavior, shown in Figure 4, is quite depending on the relative signs of κ and ϵ, as expected. One can thus freeze the tunneling (oscillations) by means of the friction in one or the other well (with $z(t) \to 1$ or -1) in a relative fast way. However, if damping is increased, with an almost racemic sample at $t = 0$, Figure 5 shows a localization in either the right or the left well due to the combined effects of κ and ϵ. The interesting point is that when $\gamma = 0$ (black oscillations), the stationary state oscillates around an average value of $z(t) \approx 0.45$. When dissipation is added, the stationary state reaches $z(t) \approx 0.75$ in a short time scale and the tunneling is completely inhibited.

In all of the cases analyzed, the corresponding stationary points are reached in a relative short period of time. Moreover, as can be easily seen in the case of $\kappa = 0$, the value of the stationary point is always greater than the average value of $z(t)$. This is the enhancement due to dissipation. Note that, although the location of the stationary points does not depend on a precise value of γ, it is only this effect which makes possible to reach such points. This result should be considered in optical activity measurements.

It is interesting to note that, although it seems plausible that $\kappa < 0$ corresponds to most probable situations (in which interactions between molecules of the same chirality are stronger than those between different isomers), the opposite situation leads to the same behavior as shown in Figure 5, even in the absence of any asymmetry. Thus, in Figure 6, the oscillations have disappeared due to dissipation and the population difference achieved is $z(t) \approx 0.9$, in contrast to the average $z(t) \approx 0.45$ when $\gamma = 0$.

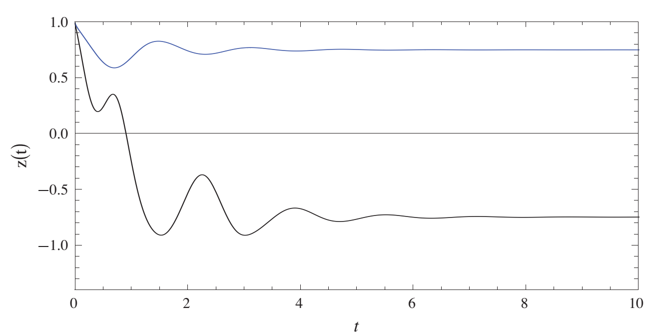

Figure 4. Same as Figure 3 with $\epsilon = 3$ (blue) and -3 (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

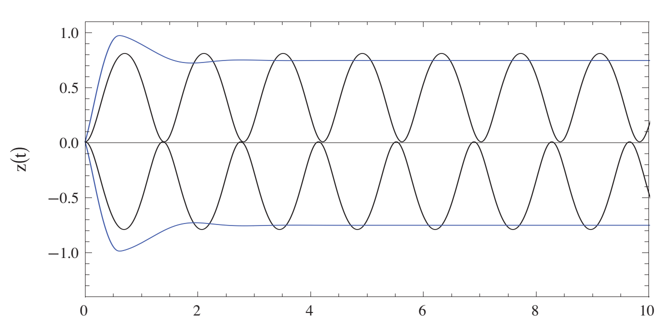

Figure 5. Localization is readily reached in presence of damping. The initial condition is racemic ($z(0) = 0.01$) with $\kappa = -5$. Top curves for $\epsilon = 3$ with $\gamma = 0.15$ (blue curve) and $\gamma = 0$ (black curve). The same for the bottom curves with $\epsilon = -3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

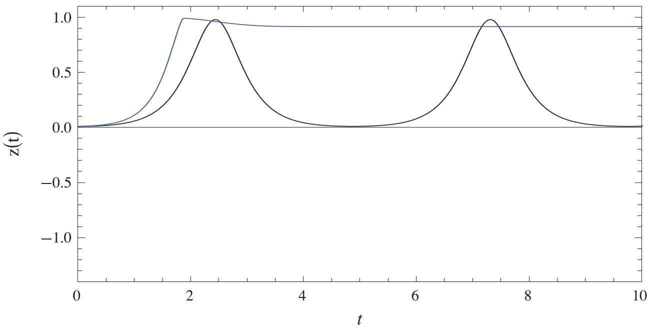

Figure 6. Localization in presence of damping with $z(0) = 0.01$, $\kappa = 5$, $\epsilon = 0, \gamma = 0.15$ (blue curve) and $\gamma = 0$ (black curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

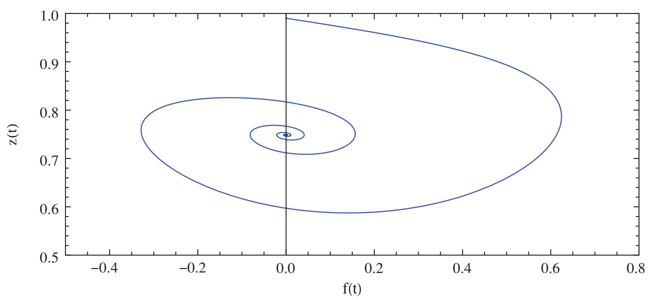

Figure 7. Phase portrait of the system of Eq. (14). We have taken $\kappa = -5, \epsilon = 3$ and $\gamma = 0.07$. See text and Figure 4 for more details.

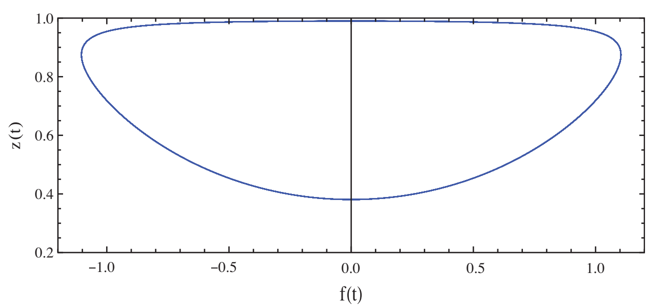

Figure 8. Same as Figure 7 but taking $\gamma = 0$.

5. Concluding remarks

In this work we have studied the competition between tunneling, parity violation (or any external chiral influence), mean–field chirality–sensitive interactions and dissipative effects in chiral molecules. By mapping the two-state dynamics into a Hamiltonian described by a pair of canonical variables (which describe the population and phase difference of chiral states), previous results by Harris and coworkers are recovered and generalized. Using the Langevin formalism, we have also extended the model to include dissipative effects by means of a Caldeira–Legget like coupling, showing that dissipation enhances the population difference when compared to a dissipation free dynamics. In addition, it has explicitly shown how dissipation blocks the tunneling process leading to non-racemic stationary states.

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Appendix

The stability around a stationary point of the dynamical system given by Eq. (14), for the bath average values of z and Φ, is quite critical depending on the parameters κ, ϵ and γ. This analysis is based on the character of the eigenvalues of the so-called stability matrix or Jacobian matrix evaluated at the stationary point. If all the eigenvalues of this matrix have non-zero real parts, the equilibrium point is said to be hyperbolic. The presence of a zero eigenvalue requires a special mathematical treatment. For our purposes, only the following theorems will be recalled in this Appendix [35]:

1. If all the eigenvalues of the Jacobian matrix of the dynamical system have negative real parts, then the corresponding equilibrium point is asymptotically stable.
2. If at least one of the eigenvalues of the Jacobian matrix has positive real part, then the equilibrium point is unstable.
3. For pure imaginary eigenvalues, linearization does not suffice. In fact, depending on the non-linear terms the equilibrium point can be unstable, stable or even asymptotically stable. In general, in two dimensions, the stability analysis is usually treated in terms of polar coordinates (periodic orbits). The stability type of a periodic orbit depends on the non-linear terms of the dynamical system. In this context, the Poincaré-Bendixson theorem guarantees under certain conditions the presence of periodic orbits around the stationary points.

Let us begin illustrating such analysis for the undamped dynamical system (8) with $\epsilon = 0$. For this case, the stationary points of (z,Φ) (issued from $\dot{z}(t) = 0$ and $\dot{\Phi}(t) = 0$) are $(0, n\pi)$ and $(\pm\sqrt{1-A^{-2}}, n\pi)$ where $A = \kappa/2\delta$. The corresponding Jacobian or stability matrices are given by:

$$J(0, n\pi) = \begin{bmatrix} 0 & -1 \\ -A + (-1)^{n+1} & 0 \end{bmatrix}$$

$$J\left(\pm\sqrt{1-A^{-2}}, n\pi\right) = \begin{bmatrix} 0 & (-1)^{n+1}A^{-2} \\ -A + (-1)^{n}A^{3} & 0 \end{bmatrix}$$

with eigenvalues for each stationary point

$$\lambda^2_{(0,n\pi)} = A + (-1)^n$$

$$\lambda^2_{(\pm\sqrt{1-A^{-2}}, n\pi)} = \frac{(-1)^{n+1}}{A} - A.$$

For positive and negative real eigenvalues, the equilibrium point, called a *saddle point*, is unstable. Pure imaginary eigenvalues appear at

- $(0, n\pi)$: $\begin{cases} \text{even } n & A < 1 \\ \text{odd } n & A < -1 \end{cases}$
- $(\pm\sqrt{1-A^{-2}}, n\pi)$: $\begin{cases} \text{even } n & A > 0 \\ \text{odd } n & A > 1 \end{cases}$

As one of the stationary points gets closer to the other, its stability will be influenced by the presence of this second stationary point, and vice versa. In this sense, it is necessary to "isolate" the stationary points. Note that for a large value of A, the value $\pm\sqrt{1-A^{-2}}$ will be closer to 1. So, the stability behavior around $(0, n\pi)$ will have less influence on the orbits around $(\pm\sqrt{1-A^{-2}}, n\pi)$.

When $\epsilon \neq 0$ in (8), the variation of the term ϵ/δ shifts the zminus coordinate of the stationary points as well as the region of stability. From the stationary conditions for z and Φ, the roots of z fulfils the equation

$$(-1)^n \frac{z}{\sqrt{1-z^2}} - \frac{\kappa}{2\delta} z - \frac{\epsilon}{\delta} = 0. \tag{19}$$

and the corresponding Φ values are the same as before. The stability analysis is carried out in a similar way leading to the same conclusions.

For the damped system (14), theorems (1) and (2) are directly applicable. With $\epsilon = 0$ and $\gamma \neq 0$, the same stationary points, $(0, n\pi)$ and $(\pm\sqrt{1-A^{-2}}, n\pi)$ are obtained. The corresponding Jacobian matrices are:

$$J(0, n\pi) = \begin{bmatrix} 2A\gamma - 2(-1)^n\gamma & (-1)^{n+1} \\ -A + (-1)^n & 0 \end{bmatrix}$$

$$J(\pm\sqrt{1-A^{-2}}, n\pi) = \begin{bmatrix} 2\gamma A - 2\gamma(-1)^n A^3 & (-1)^{n+1} A^{-1} \\ -A + (-1)^n A^3 & 0 \end{bmatrix},$$

with eigenvalues given by

$$\lambda_{(0,n\pi)} = \gamma(A + (-1)^{n+1}) \pm \sqrt{D_1}/2$$

$$\lambda_{(\pm\sqrt{1-A^{-2}}, n\pi)} = \gamma A(1 + (-1)^{n+1} A^2) \pm \sqrt{D_2}/2,$$

where

$$D_1 = 4\gamma^2 \left[A + (-1)^{n+1}\right] - 4(-1)^n (A+1)$$

$$D_2 = 4\gamma^2 A^2 \left[1 + (-1)^{n+1} A^2\right]^2 - 4((-1)^{n+1} + A^2).$$

According to theorems (1) and (2), we have asymptotic stability around the stationary points when:

- $(0, n\pi)$: $\begin{cases} \text{even } n & A < 1 \\ \text{odd } n & A < -1 \end{cases}$
- $(\pm\sqrt{1-A^{-2}}, n\pi)$: $\begin{cases} \text{even } n & -1 < A < 0 \text{ or } A > 1 \\ \text{odd } n & A < 0 \end{cases}$

For even n and $A = 1$, the stationary points accumulates at $(0, n\pi)$ and the real part of the eigenvalues becomes null. The asymptotic stability behavior is identified with spirals approaching the equilibrium point in the phase portraits.

Finally, when $\epsilon \neq 0$, the stationary point is going to be asymptotically stable as $t \to \infty$ (see Figure 7). This is the main difference with the undamped system which may describe periodic orbits (see Figure 8).

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