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Long-range retarded intermolecular forces

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The retarded interactions between neutral molecules at very large separations are calculated by perturbation of the electromagnetic vacuum state. This state is represented by the Wheeler form of the electromagnetic vacuum functional. Besides the well-known Casimir attractive R^{-7} potential energy between polarizable bodies, the repulsive interaction between one electrically and one magnetically polarizable molecule proportional to R^{-7} is computed. Also the specific discriminating force between optically active molecules, with potential proportional to R^{-9}, is shown to follow similar calculations. For isomeric molecules this force is repulsive for identical handedness and attractive between enantiomers.

I. INTRODUCTION

It has been known since the early work of Casimir[1] that the forces between electrically neutral systems are considerably changed at very distant separations from that deducible from Coulomb's law between the constituent charges. In the case of electrically polarizable bodies the potential energy of the interbody force at these large distances is

$$V_{E-E}(R) = -\frac{23}{4\pi}\hbar c\,\frac{\alpha(a)\alpha(b)}{R^7}, \tag{1}$$

for isotropic polarizabilities $\alpha(a)$ and $\alpha(b)$ of the two bodies. This form of potential energy takes over from the London energy, proportional to R^{-6} and obtained by applying perturbation theory with the inter-Coulomb energies, at separations R much larger than the wavelengths associated with the natural frequencies of (a) and (b). In the case of a simple atom such frequencies correspond to the energies of excited electronic states above the ground state. There are several reviews[2-4] that summarize the long-range intermolecular forces in these simple cases. In the domain where Eq. (1) is valid the polarizable bodies are passive: It is the fluctuating electromagnetic field that is dynamically responsible for the energy shifts. Recently I showed[5] how the energy (1) can be obtained from perturbations changing the vacuum state of quantum electrodynamics. This state has wave functional

$$\Psi_0[\vec{B}] = N\exp\left(-\frac{1}{16\pi^3\hbar c}\int\int\frac{\vec{B}(\vec{r})\cdot\vec{B}(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|^2}\,d^3r\,d^3r'\right) \tag{2}$$

as shown by Wheeler.[6] The perturbations that change the energy Z_0 of the vacuum state are due to the presence of the polarizable bodies. In the present paper the same idea has been used to obtain long-range interactions due to other characteristics of the atoms or molecules. In particular the energy law[7,8]

$$V_{E-M} = +\frac{7}{4\pi}\hbar c\,\frac{\alpha_E(a)\alpha_M(b)}{R^7}, \tag{3}$$

that gives a repulsive force between electric body (a) and body (b) with magnetic polarization $\alpha_M(b)$, is shown to follow immediately. Of more interest the specific intermolecular energies between disymmetric molecules, specific as between enantiomers, can be deduced by similar arguments. This goes beyond the two aforementioned R^{-7} laws, and the reasoning that leads to a potential proportional to R^{-9} in this case is presented on simple dimensional grounds. The numerical constants of proportionality are harder to compute but it is shown that, if each molecule has one strong electronic level, E_a, E_b, that absorbs differentially between left and right circularly polarized light, the discriminating energy is

$$V_{\text{disc}}(R) = +\frac{16}{3\pi}\frac{R(a)R(b)}{E_a^2E_b^2}\frac{(\hbar c)^3}{R^9}, \tag{4}$$

where $R(a)$ and $R(b)$ are the optical rotatory strengths at the levels E_a and E_b for the two molecules. It is of interest to note that similarly handed molecules repel through (4) but molecules of opposing handedness attract. This basic difference also occurs for the London region too.[9] Unfortunately, in both cases, the discriminating forces are very weak compared with the equal nondiscriminating forces that arise from electric polarizabilities alone.

II. METHOD

The method employed below to calculate the relevant energy shifts is based on changing the vacuum energy of the radiation field by the presence of the molecules and isolating that shift which depends on the relative position of the molecule pair. The calculation of the shifts is by perturbation theory—but with no response of the matter. In one obvious sense the method is complementary to that involved in calculating energy shifts in external passive fields. Complete quantum electrodynamics can be considered as a dynamics based on the Hamiltonian

$$H_{\text{tot}} = H_{\text{rad}}(\vec{E}^{\perp}, \vec{A}) + H_{\text{mat}}(p, q) + H_{\text{int}}(\vec{E}^{\perp}, \vec{A}; p, q), \tag{5}$$

a functional of the canonical pairs $(\vec{E}^{\perp}, \vec{A})$ and (p_α, q_α), $\alpha = 1, 2, \ldots, n$. On the other hand the elementary quantum theory of molecules in given external fields has Hamiltonian

$$H_M = H_{\text{mat}}(p, q) + H_{\text{int}}(p, q), \tag{6}$$

where the canonical pairs of the charges (p_α, q_α) alone are dynamically operative. H_{int} depends on the electromagnetic fields in a parametric way but there are no field equations for the electromagnetic field to be obtained from H_M. The point of view taken here is to consider

$$H_F = H_{\text{rad}}(\vec{E}^{\perp}, \vec{A}) + H_{\text{int}}(\vec{E}^{\perp}, \vec{A}) \tag{7}$$

as the Hamiltonian of the dynamical system. The canonical pair $(\vec{E}^{\perp}, \vec{A})$ stands alone and H_{int} depends parametrically on the molecules or atoms which are passive. No field equations for matter are to be obtained from H_F.

From the work of Wheeler^6 (see also Kuchař^{10}) the ground-state functional of H_{rad} in the "q" representation is given by Eq. (2). We apply standard perturbation theory to calculate energy shifts due to H_{int}. In particular for two-body forces we assume

$$H_{\text{int}}(\vec{E}^{\perp}, \vec{A}) = H_{\text{int}}^{(a)}(\vec{E}^{\perp}, \vec{A}) + H_{\text{int}}^{(b)}(\vec{E}^{\perp}, \vec{A}), \tag{8}$$

so that the field interacts with (a) and (b) separately. Then the shift ΔE, from the unperturbed value, that depends on the relative position is (in lowest nonvanishing order)

$$\Delta E = \langle \Psi_0 | H_{\text{int}}^{(a)} \frac{1}{Z_0 - H_{\text{rad}}} H_{\text{int}}^{(b)} | \Psi_0 \rangle + \langle \Psi_0 | H_{\text{int}}^{(b)} \frac{1}{Z_0 - H_{\text{rad}}} H_{\text{int}}^{(a)} | \Psi_0 \rangle . \tag{9}$$

The calculations then depend on evaluating the functional integrals in

$$\begin{aligned}\Delta E = -2 \int \exp\left(-\frac{1}{16\pi^3 \hbar c} \int\int \frac{\vec{B}(\vec{r})\cdot\vec{B}(\vec{r}')}{|\vec{r}-\vec{r}'|^2} d^3r\, d^3r'\right) H_{\text{int}}^{(a)}(\vec{E}^{\perp}, \vec{B}) \\ \times \left(\frac{1}{8\pi}\int (\vec{E}^2 + \vec{B}^2) d^3r - Z_0\right)^{-1} H_{\text{int}}^{(b)}(\vec{E}^{\perp}, \vec{B}) \exp\left(-\frac{1}{16\pi^3 \hbar c} \int\int \frac{\vec{B}(\vec{r})\cdot\vec{B}(\vec{r}')}{|\vec{r}-\vec{r}'|^2} d^3r\, d^3r'\right) d\vec{B} \Big/ \\ \int \exp\left(-\frac{1}{8\pi^3 \hbar c} \int\int \frac{\vec{B}(\vec{r})\cdot\vec{B}(\vec{r}')}{|\vec{r}-\vec{r}'|^2} d^3r\, d^3r'\right) d\vec{B},\end{aligned} \tag{10}$$

where

$$E_i(\vec{r}) \to 4\pi i \hbar c \epsilon_{ijk} \nabla_k \frac{\delta}{\delta B_j(\vec{r})}, \tag{11}$$

since

$$[E_i(\vec{r}), B_j(\vec{r}')] = 4\pi i \hbar c \epsilon_{ijk} \nabla_k \delta(\vec{r} - \vec{r}') . \tag{12}$$

In going from Eq. (9) to (10) we use the Hermitian nature of H_{int} and express the normalization factor N^{-2} explicitly.

III. CALCULATIONS

To proceed further and evaluate Eq. (10) it is necessary to know $H_{\text{int}}^{(a)}$ and $H_{\text{int}}^{(b)}$. For the first of the three cases mentioned in the Introduction we have simple isotropic electrically polarizable systems so that

$$H_{\text{int}}^{(a)} = -\tfrac{1}{2}\alpha(a)\vec{E}^2(a) \tag{13}$$

and

$$H_{\text{int}}^{(b)} = -\tfrac{1}{2}\alpha(b)\vec{E}^2(b) . \tag{14}$$

As discussed in Ref. 5 it is easier to calculate in the "p" representation for Ψ_0 and a simple scaling

$$\vec{B} = (\hbar c)^{1/2}\mathcal{B}; \quad \vec{E} = (\hbar c)^{1/2}\vec{\mathcal{E}} \tag{15}$$

gives the energy shift in this case to be

$$V_{E-E}(R) = -\alpha(a)\alpha(b)\hbar c \times \frac{\frac{1}{2}\int \exp(-I)\vec{\mathcal{E}}^2(a)\Delta^{-1}\vec{\mathcal{E}}^2(b)\exp(-I)d\vec{\mathcal{E}}}{\int \exp(-2I)d\vec{\mathcal{E}}}, \tag{16}$$

where

$$I = \frac{1}{16\pi^3} \int \frac{\vec{\mathcal{E}}(\vec{r})\cdot\vec{\mathcal{E}}(\vec{r}')}{|\vec{r}-\vec{r}'|^2} d^3r\, d^3r' \tag{17}$$

and

$$\Delta = \frac{1}{8\pi}\int (\vec{\mathcal{E}}^2 + \vec{\mathcal{B}}^2) d^3r - \frac{Z_0}{\hbar c} . \tag{18}$$

I is clearly a number, $\vec{\mathcal{E}}$ and $\vec{\mathcal{B}}$ have dimensions $(\text{length})^{-2}$, and Δ has dimension $(\text{length})^{-1}$. If we count the dimensions of the numerator functional integral we find $(\text{length})^{-4+1-4-2}$ while the denominator has dimensions $(\text{length})^{-2}$, hence, since the sole length in the problem is the separation distance R between the molecules

$$V_{E-E}(R) = -\frac{\alpha(a)\alpha(b)\hbar c}{R^7} \times (\text{number}). \tag{19}$$

In the second case where body (a) is electrically polarizable and body (b) is magnetically polarizable we use

$$H_{\text{int}}^{(a)} = -\tfrac{1}{2}\alpha_E(a)\vec{\mathrm{E}}^2(a) \tag{20}$$

and

$$H_{\text{int}}^{(b)} = -\tfrac{1}{2}\alpha_M(b)\vec{\mathrm{B}}^2(b). \tag{21}$$

Clearly the same dimensional argument goes through as before and again we have a potential energy proportional to R^{-7}

$$V_{E-M}(R) = -\alpha_E(a)\alpha_M(b)\hbar c\, \frac{\frac{1}{2}\int \exp(-I)\vec{\mathcal{E}}^2(a)\Delta^{-1}\vec{\mathcal{B}}^2(b)\exp(-I)\,d\vec{\mathcal{E}}}{\int \exp(-2I)\,d\vec{\mathcal{E}}} \tag{22}$$

$$= -\frac{\alpha_E(a)\alpha_M(b)\hbar c}{R^7} \times (\text{another number}). \tag{23}$$

Finally in the case of optically active molecules the interaction Hamiltonian is more complicated. In the Appendix it is shown that, for randomly oriented molecules,

$$H_{\text{int}}^{(a)} = -\frac{1}{3}\frac{R(a)}{E_a^2}\hbar c(\vec{\mathrm{E}}\cdot\text{curl}\vec{\mathrm{E}} + \vec{\mathrm{B}}\cdot\text{curl}\vec{\mathrm{B}}) \tag{24}$$

and

$$H_{\text{int}}^{(b)} = -\frac{1}{3}\frac{R(b)}{E_b^2}\hbar c(\vec{\mathrm{E}}\cdot\text{curl}\vec{\mathrm{E}} + \vec{\mathrm{B}}\cdot\text{curl}\vec{\mathrm{B}}) \tag{25}$$

with $R(a)$ and $R(b)$ the optical rotatory strengths at active frequencies $E_a/\hbar$ and $E_b/\hbar$. The discriminating energy can now be written down from Eq. (10) as

$$V_{\text{disc}}(R) = -\frac{R(a)R(b)(\hbar c)}{E_a^2 E_b^2}\,\frac{2}{9}\int \exp(-I)[\vec{\mathrm{E}}(a)\cdot\text{curl}\vec{\mathrm{E}}(a) + \vec{\mathrm{B}}(a)\cdot\text{curl}\vec{\mathrm{B}}(a)]$$

$$\times\frac{\Delta^{-1}[\vec{\mathrm{E}}(b)\cdot\text{curl}\vec{\mathrm{E}}(b) + \vec{\mathrm{B}}(b)\cdot\text{curl}\vec{\mathrm{B}}(b)]\exp(-I)\,d\vec{\mathrm{E}}}{\int \exp(-2I)\,d\vec{\mathrm{E}}}. \tag{26}$$

A count of the length dimensions in these functional integrals leads at once to the dependency of R^{-9}. So that

$$V_{\text{disc}}(R) = -\frac{R(a)R(b)}{E_a^2 E_b^2}\,\frac{(\hbar c)^3}{R^9} \times (\text{another number}). \tag{27}$$

Using a large but finite quantization box one may convert these functional integrals in Eqs. (16), (22), and (26) into mode summations, equivalent to two photons of wave vectors $\vec{\mathrm{k}}$ and $\vec{\mathrm{k}}'$. For the number in Eq. (19) we have

$$\frac{R^7}{(2\pi)^4}\int \frac{k^3 k'^3}{(k+k')}[1 + (\hat{k}\cdot\hat{k}')^2]\cos[(\vec{\mathrm{k}}+\vec{\mathrm{k}}')\cdot\vec{\mathrm{R}}]\,dk\,dk'\,d\Omega\,d\Omega' = \frac{23}{4\pi}, \tag{28}$$

while that for Eqs. (22) and (23) is

$$\frac{R^7}{(2\pi)^4}\int \frac{k^3 k'^3}{(k+k')}\,2\hat{k}\cdot\hat{k}'\cos[(\vec{\mathrm{k}}+\vec{\mathrm{k}}')\cdot\vec{\mathrm{R}}]\,dk\,dk'\,d\Omega\,d\Omega' = -\frac{7}{4\pi}. \tag{29}$$

Finally for the discriminating energy of Eqs. (26) and (27) the constant of proportionality is

$$\frac{R^9}{9(2\pi)^4}\int \frac{k^3 k'^3 (k'-k)^2}{(k+k)}[1 + (\hat{k}\cdot\hat{k}')^2 + 2\hat{k}\cdot\hat{k}']\cos[(\vec{\mathrm{k}}+\vec{\mathrm{k}}')\cdot\vec{\mathrm{R}}]\,dk\,dk'\,d\Omega\,d\Omega' = -\frac{16}{3\pi}. \tag{30}$$

With these numerical values in Eqs. (19), (23), and (27) the retarded interaction potentials quoted in the Introduction follow.

APPENDIX

It is well known[11] that the conventional nonrelativistic Hamiltonian for neutral molecules interacting with radiation, namely,

$$H=\sum_{\alpha}\frac{[\vec{p}_\alpha-e_\alpha\vec{A}(q_\alpha)/c]^2}{2m_\alpha}+V_{\text{Coul}}+H_{\text{rad}}, \qquad \text{(A1)}$$

can be transformed, and the $e\vec{p}\cdot\vec{A}/c$ terms eliminated, by the canonical transformation $e^{-iS}He^{+iS}$ with $S=(e/\hbar c)\int\vec{q}\cdot\vec{A}d^3r$. The simplest form of the transformed Hamiltonian is

$$H_{\text{tot}}=H_{\text{mol}}+H_{\text{rad}}-\int\vec{p}(\vec{r})\cdot\vec{E}^{\perp}(\vec{r})d^3r$$
$$-\int\vec{m}(\vec{r})\cdot\vec{B}(\vec{r})d^3r\,. \qquad \text{(A2)}$$

In Eq. (A2), $\vec{p}(\vec{r})$ and $\vec{m}(\vec{r})$ are the electric and magnetic polarization fields, respectively. In dipole approximation

$$\vec{p}(\vec{r})=\vec{\mu}(a)\delta(\vec{r}-\vec{R}_a)+\vec{\mu}(b)\delta(\vec{r}-\vec{R}_b)$$

and (A3)

$$\vec{m}(\vec{r})=\vec{m}(a)\delta(\vec{r}-\vec{R}_a)+\vec{m}(b)\delta(\vec{r}-\vec{R}_b)\,.$$

Equation (A2) has been obtained[12] by ignoring the diamagnetic interactions quadratic in the magnetic field and certain field independent-energy shifts of the form $\int(\vec{p}^{\perp})^2d^3r$.

In this Appendix a further canonical transformation is carried out generated by T, i.e.,

$$H_{\text{new}}=e^{-iT}H_{\text{tot}}\,e^{iT}, \qquad \text{(A4)}$$

which eliminates the $H_{\text{int}}=-\mu\cdot\vec{E}-\vec{m}\cdot\vec{B}$ terms in (A2). It is clear that if T is chosen so that

$$-i[T,H_{\text{mol}}]+H_{\text{int}}=0, \qquad \text{(A5)}$$

then, to second order in e,

$$H_{\text{new}}=H_{\text{mol}}+H_{\text{rad}}-\tfrac{1}{2}i[T,H_{\text{int}}]-i[T,H_{\text{rad}}]$$
$$-\tfrac{1}{2}[T,[T,H_{\text{rad}}]]\cdot \qquad \text{(A6)}$$

The m-n matrix element for T that solves (A5) is

$$T_{mn}=-\frac{i\vec{\mu}^{mn}\cdot\vec{E}}{E_{mn}}-\frac{i\vec{m}^{mn}\cdot\vec{B}}{E_{mn}}. \qquad \text{(A7)}$$

With this choice of T the m-o matrix element of $-i/2[T,H_{\text{int}}]$ is

$$\frac{1}{2}\left(\frac{1}{E_{mn}}-\frac{1}{E_{n0}}\right)(\mu_i^{mn}\mu_j^{no}E_iE_j+m_i^{mn}m_j^{no}B_iB_j$$
$$+\mu_i^{mn}m_j^{no}E_iB_j+m_j^{mn}\mu_i^{no}B_jE_i)\,. \qquad \text{(A8)}$$

If the transition moments are expressed in body-fixed axes λ, μ, $\nu=1, 2$, or 3, we have

$$\mu_i=R_{i\lambda}\mu_\lambda\,,\quad m_i=R_{i\lambda}m_\lambda\,, \qquad \text{(A9)}$$

where $R_{i\lambda}$ is the Eulerian matrix. The random average of $R_{i\lambda}R_{j\mu}$ is

$$\langle R_{i\lambda}R_{j\mu}\rangle=\tfrac{1}{3}\delta_{ij}\delta_{\lambda\mu} \qquad \text{(A10)}$$

and the diagonal term $o=m$ of (A8) becomes

$$-\frac{1}{3}\frac{\vec{\mu}^{on}\cdot\vec{\mu}^{no}}{E_{no}}\vec{E}^2-\frac{1}{3}\frac{\vec{m}^{on}\cdot\vec{m}^{no}}{E_{no}}\vec{B}^2-\frac{1}{3}\frac{\vec{\mu}^{on}\cdot\vec{m}^{no}}{E_{no}}(\vec{E}\cdot\vec{B}-\vec{B}\cdot\vec{E})$$
$$\text{(A11)}$$

$$=-\tfrac{1}{2}\alpha_E\vec{E}^2-\tfrac{1}{2}\alpha_M\vec{B}^2\,. \qquad \text{(A12)}$$

The term in (A6) that gives rise to the $H_{\text{int}}^{(a)}$ and $H_{\text{int}}^{(b)}$ of Eqs. (24) and (25) is $-\frac{1}{2}[T, [T, H_{\text{rad}}]]$ (The remaining term $i[T,H_{\text{rad}}]$ is needed to give single absorption and emission of photons.) The general m-o matrix element of $-\frac{1}{2}[T, [T, H_{\text{rad}}]]$ is, using Eq. (12),

$$+\tfrac{1}{2}i\hbar c\epsilon_{ijk}\left(\frac{E_l\nabla_kE_j}{E_{mn}E_{no}}(\mu_l^{mn}m_i^{no}-m_i^{mn}\mu_l^{no})\right.$$
$$-\frac{B_l\nabla_kB_j}{E_{mn}E_{no}}(m_l^{mn}\mu_i^{no}-\mu_i^{mn}m_l^{no})$$
$$\left.+\text{terms in }|\vec{\mu}|^2\text{ and }|\vec{m}|^2\right)\,. \qquad \text{(A13)}$$

The latter terms in (A13) are higher-order contributions to the polarization effects of (A12) and the mixed terms in (A13) have the diagonal ($o=m$) contribution

$$-i\hbar c(\epsilon_{ijk}/E_{on}^2)(E_l\nabla_kE_j\mu_l^{on}m_i^{no}+B_l\nabla_kB_j\mu_i^{on}m_l^{no})\,.$$
$$\text{(A14)}$$

Again if the random orientation average is taken of (A14) using (A10) this term is

$$(i\hbar c/3E_{no}^2)\langle o|\vec{\mu}|n\rangle\cdot\langle n|\vec{m}|o\rangle\,(\vec{E}\cdot\text{curl}\vec{E}+\vec{B}\cdot\text{curl}\vec{B})\,.$$
$$\text{(A15)}$$

Finally, since the optical rotatory strength in the dipole approximation is

$$R_{no}=\text{Im}\langle o|\vec{\mu}|n\rangle\cdot\langle n|\vec{m}|o\rangle\,, \qquad \text{(A16)}$$

the effective interaction energy for molecule (a) is

$$H_{\text{int}}^{(a)}=-[R_{no}(a)\hbar c/3E_{no}^2](\vec{E}\cdot\text{curl}\vec{E}+\vec{B}\cdot\text{curl}\vec{B})\,.$$
$$\text{(A17)}$$

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