PHYSICAL REVIEW A VOLUME 51, NUMBER 5 MAY 1995

Dispersion forces between molecules with one or both molecules excited

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(Received 14 October 1994)

Dispersion energies between molecules involving one in an electronically excited state are calculated using fourth-order perturbation theory within the framework of the multipolar form of quantum electrodynamics. There are significant differences between the energies for these cases and those where both molecules are in their ground states. The calculations are performed within the electric-dipole approximation for the interaction of the molecules with the electromagnetic field. The energies found are valid for all separations beyond the electronic overlap region. The results of previous investigations are shown to be incomplete and the origin of the incompleteness is traced to the neglect of certain real-photon contributions. The energies obtained in this paper are in agreement with our earlier calculations based on a form of response theory. They are made up of two types: one resulting from virtual-photon exchange and the other from real photons. The virtual-photon term has the same structure as the Casimir-Polder potential for ground-state molecules. The real-photon term is a polynomial in the inverse intermolecular separation R^{-1}, in contrast to the modulated contributions in the previous incomplete investigations. The asymptotic forms for the total energy are discussed. The far-zone behavior is dominated by the real-photon term and shows an R^{-2} dependence. The near-zone behavior shows an R^{-6} dependence, arising in the multipolar formalism from both virtual- and real-photon exchange.

PACS number(s): 34.20.Cf, 33.80.Ps, 12.20.−m

I. INTRODUCTION AND THEORY

The dispersion interaction between two nonpolar molecules separated by a distance R beyond electron overlap has been studied extensively when both molecules are in their ground states. In the electric-dipole approximation the interaction energy shows an R^{-6} dependence for R smaller than the wavelengths of molecular electronic transitions, and R^{-7} for much larger distances. For a pair of randomly oriented molecules A and B, the former is given by the well-known London formula [1]

$$V_{\text{London}}(R)=-\tfrac{2}{3}\sum_{r,s}\frac{|\mu^{0r}(A)|^2|\mu^{0s}(B)|^2}{(E_{r0}+E_{s0})R^6}\ , \qquad (1.1)$$

where $\vec{\mu}^{0r}(A)$ and $\vec{\mu}^{0s}(B)$ are the transition dipole moments, and E_{r0} and E_{s0} are the transition energies for the transitions $r\leftarrow 0$ and $s\leftarrow 0$. The interaction energy at long range can be expressed in terms of the static polarizabilities of the molecules. It is [2]

$$V_{\text{Casimir}}(R)=-\frac{23\hbar c}{4\pi}\frac{\alpha(A)\alpha(B)}{R^7}\ . \qquad (1.2)$$

The full interaction energy for which (1.1) and (1.2) are the asymptotic limits was obtained by Casimir and Polder [3] using quantum electrodynamics. It may be expressed as an integral over an imaginary wave number u, namely,

$$\begin{aligned}V(R)&=-\frac{\hbar c}{2\pi}\int_0^\infty \alpha^A(icu)\alpha^B(icu)\left[(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{e^{-uR}}{R}\right]\left[(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{e^{-uR}}{R}\right]du\\&=-\frac{\hbar c}{\pi}\int_0^\infty \alpha^A(icu)\alpha^B(icu)u^6e^{-2uR}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right]du\ ,\end{aligned} \qquad (1.3)$$

where

$$\alpha(icu)=\frac{2}{3\hbar c}\sum_n\frac{k_{n0}|\mu^{n0}|^2}{(k_{n0}^2+u^2)} \qquad (1.4)$$

is the polarizability at the imaginary frequency cu. An alternative expression for $V(R)$ in terms of the combinations of sine and cosine integral functions $\mathrm{si}(x)$ and $\mathrm{ci}(x)$ [4]

$$\begin{aligned}f(x)&=\mathrm{ci}(x)\sin x-\mathrm{si}(x)\cos x\ ,\\g(x)&=-\mathrm{ci}(x)\cos x-\mathrm{si}(x)\sin x\ ,\end{aligned} \qquad (1.5)$$

1050-2947/95/51(5)/3660(7)/$06.00

is

$$V(R)=-\frac{2}{9\pi\hbar c}\sum_{r,s}\frac{|\vec{\mu}^{0r}(A)|^2|\vec{\mu}^{0s}(B)|^2}{k_{r0}^2-k_{s0}^2}\left\{(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{R}\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}\right.$$
$$\left.\times[k_{r0}f(k_{s0}(R+\bar{R}))-k_{s0}f(k_{r0}(R+\bar{R}))]\right\}_{\bar{R}=R}, \tag{1.6}$$

where $\bar{R}$ has been introduced to separate differentiations. After differentiating and putting $\bar{R}$ equal to R, we obtain

$$V(R)=-\frac{2}{9\pi\hbar c}\sum_{r,s}\frac{|\vec{\mu}^{0r}(A)|^2]^{0s}(B)|^2}{R^2}\frac{k_{r0}k_{s0}}{k_{r0}^2-k_{s0}^2}$$
$$\times\left\{k_{r0}^3\left[\frac{1}{k_{r0}R}-f(2k_{r0}R)\left[2-\frac{10}{k_{r0}^2R^2}+\frac{6}{k_{r0}^4R^4}\right]+g(2k_{r0}R)\left[\frac{4}{k_{r0}R}-\frac{12}{k_{r0}^3R^3}\right]\right]\right.$$
$$\left.-k_{s0}^3\left[\frac{1}{k_{s0}R}-f(2k_{s0}R)\left[2-\frac{10}{k_{s0}^2R^2}+\frac{6}{k_{s0}^4R^4}\right]+g(2k_{s0}R)\left[\frac{4}{k_{s0}R}-\frac{12}{k_{s0}^3R^3}\right]\right]\right\}. \tag{1.7}$$

When one or both molecules are excited, the interaction is significantly different from the above. One important difference is that the force between the molecules can be either attractive or repulsive in contrast to the force between ground-state molecules which is always attractive. This is easily seen in the small-R limit from the formula analogous to (1.1) which for the excited state $|m\rangle$ of A reads

$$V(R)=-\frac{2}{3}\sum_{r,s}\frac{|\vec{\mu}^{mr}(A)|^2|\vec{\mu}^{0s}(B)|^2}{(E_{s0}-E_{mr})R^6}. \tag{1.8}$$

For some downward transitions $(E_{s0}-E_{mr})$ can be negative and the resulting $V(R)$ may be positive. As we shall see in Sec. II, downward transitions lead at large separations to an R^{-2} potential of either sign. In this paper we determine the complete interaction potential at all separations for such pairs and contrast these potentials with those for ground-state pairs. We show that previous investigations [5–7] are incomplete and the correct results obtained here using perturbation theory in quantum electrodynamics agree with our earlier calculations [8,9] using a form of response theory.

The starting point for these calculations is the multipolar Hamiltonian (1.9) for the interaction of the molecules with the electromagnetic field. In the electric-dipole approximation we have

$$H=H_A+H_B+H_{\text{rad}}+H_{\text{int}}, \tag{1.9}$$

where

$$H_{\text{int}}=-\vec{\mu}(A)\cdot\vec{d}(\vec{R}_A)-\vec{\mu}(B)\cdot\vec{d}(\vec{R}_B), \tag{1.10}$$

where $\vec{d}(\vec{r})$ is the Maxwell displacement vector field operator. In the multipolar formalism, the intermolecular coupling between two neutral molecules is entirely due to transverse photon exchange. The leading contribution to the energy shift for a pair of nonpolar molecules is found using fourth-order perturbation theory,

$$\Delta E_i=-\sum_{\text{I,II,III}}\frac{\langle i|H_{\text{int}}|\text{III}\rangle\langle\text{III}|H_{\text{int}}|\text{II}\rangle\langle\text{II}|H_{\text{int}}|\text{I}\rangle\langle\text{I}|H_{\text{int}}|i\rangle}{(E_{\text{I}}-E_i)(E_{\text{II}}-E_i)(E_{\text{III}}-E_i)} \tag{1.11}$$

for the unperturbed state $|i\rangle$. Evaluation of (1.11) is facilitated with the use of time-ordered diagrams.

II. INTERACTION BETWEEN A GROUND-STATE MOLECULE AND AN ELECTRONICALLY EXCITED MOLECULE

We consider two nonidentical molecules A and B, and take A to be in the excited state $|m\rangle$ and B to be in its ground state. The unperturbed state $|i\rangle$ is then $|E_m^A,E_0^B;0\rangle$ where the electromagnetic field is in the vacuum state. For contributions to the shift (1.11) from intermediate states of A lying above $|m\rangle$, the calculations are identical to those for the ground state. The result has the same structure as (1.7) with μ^{r0} replaced by μ^{rm}, k_{r0} by k_{rm}, and the r sum restricted to $E_r>E_m$. The significant differences from the ground-state result arise from downward transitions of A. These differences are conveniently studied by confining our attention to one downward transition of A and one upward transition of B. The complete result is easily obtained by generalizing this two-level model. We denote the downward transition energy of A by $\hbar ck_A$ and the upward transition energy of B by $\hbar ck_B$. The associated transition moments are denoted by $\vec{\mu}(A)$ and $\vec{\mu}(B)$ and, without loss of generality, taken to be real. The 12 topologically distinct time-ordered diagrams for this case are shown in Fig. 1 and their associated energy denominators in Table I. It should be noted that, in contrast to the ground-state case, the denominators can vanish for those graphs where

TABLE I. Denominators D_α in Eq. (2.6).

Graph	1/denominator
(i)	$1/(p+k_B)(p+p')(p'-k_A+i\varepsilon)$
(ii)	$1/(p'+k_B)(p+p')(p'-k_A+i\varepsilon)$
(iii)	$1/(p+k_B)(k_B-k_A)(p'-k_A+i\varepsilon)$
(iv)	$1/(p+k_B)(k_B-k_A)(p'+k_B)$
(v)	$1/(p'+k_B)(p+p'+k_B-k_A)(p'-k_A+i\varepsilon)$
(vi)	$1/(p'+k_B)(p+p'+k_B-k_A)(p+k_B)$
(vii)	$1/(p-k_A-i\varepsilon)(p+p')(p'+k_B)$
(viii)	$1/(p-k_A-i\varepsilon)(p+p')(p+k_B)$
(ix)	$1/(p-k_A-i\varepsilon)(k_B-k_A)(p'+k_B)$
(x)	$1/(p-k_A-i\varepsilon)(k_B-k_A)(p'-k_A+i\varepsilon)$
(xi)	$1/(p-k_A-i\varepsilon)(p+p'+k_B-k_A)(p+k_B)$
(xii)	$1/(p-k_A-i\varepsilon)(p+p'+k_B-k_A)(p'-k_A+i\varepsilon)$

real-photon emission or absorption is possible. The corresponding singularities in the integrals over the virtual-photon momenta $\vec p$ and $\vec p\,'$ are dealt with by the prescription of adding $\pm i\varepsilon$ depending on whether a real photon can be emitted or absorbed. This corresponds to giving a spectral width to the excited state $|m\rangle$ of A. To carry out the virtual-photon integrations, we use the identity

$$\frac{1}{x\pm i\varepsilon}=\frac{\mathrm{P}}{x}\mp i\pi\delta(x) \tag{2.1}$$

and the product identity

$$\frac{1}{x-i\varepsilon}\,\frac{1}{y+i\varepsilon}=\frac{\mathrm{P}}{x}\frac{\mathrm{P}}{y}+\pi^2\delta(x)\delta(y)+i\pi\left[\frac{\mathrm{P}}{y}\delta(x)-\frac{\mathrm{P}}{x}\delta(y)\right]. \tag{2.2}$$

We now examine the contribution from diagram (i) to the energy shift. The relevant intermediate states for this diagram are

$$\begin{aligned}|\mathrm{I}\rangle&=|0,0;(\vec p\,',\lambda')\rangle\,,\\|\mathrm{II}\rangle&=|k_A,0;(\vec p,\lambda),(\vec p\,',\lambda')\rangle\,,\\|\mathrm{III}\rangle&=|k_A,k_B;(\vec p,\lambda)\rangle\,,\end{aligned} \tag{2.3}$$

where $(\vec p,\lambda)$ and $(\vec p\,',\lambda')$ are the virtual-photon modes with momenta $\vec p$ and $\vec p\,'$, and polarization labels λ and λ'. With the aid of these states (2.3) and the interaction Hamiltonian (1.10), this contribution is found to be

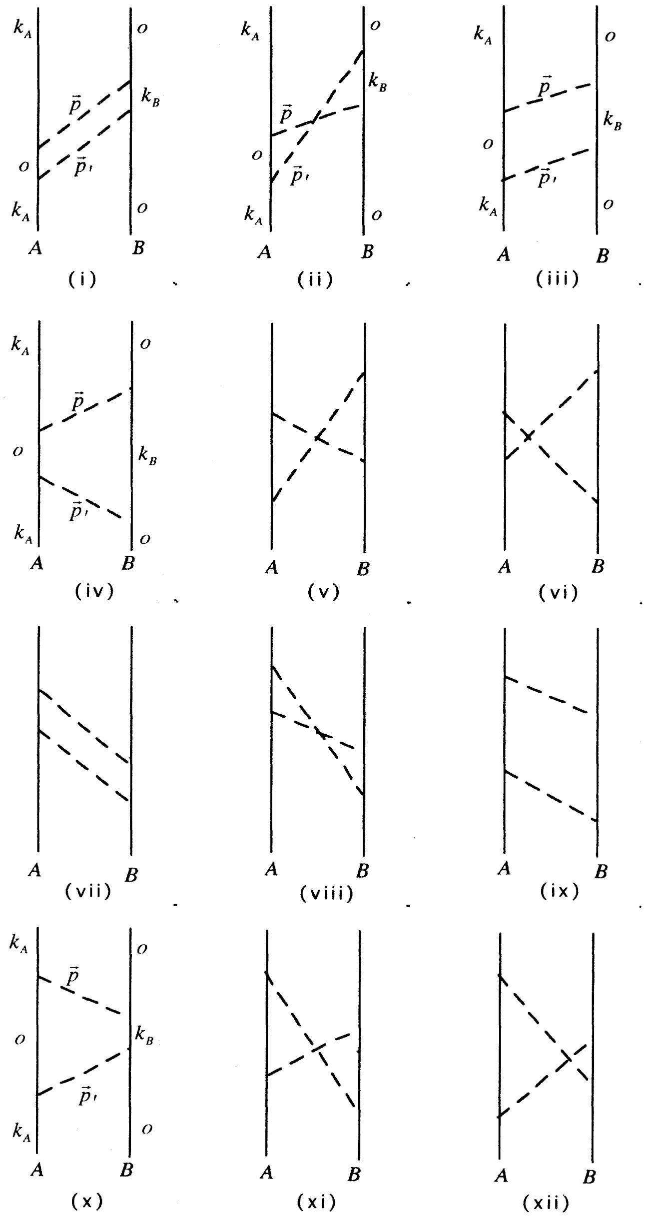

FIG. 1. Time-ordered diagrams for two-photon exchange between an excited- and a ground-state molecule.

$$-\mu_i(A)\mu_j(A)\mu_k(B)\mu_l(B)\sum_{\substack{\vec p,\lambda\\ \vec p\,',\lambda'}}\left[\frac{2\pi\hbar c p}{V}\right]\left[\frac{2\pi\hbar c p'}{V}\right]\bar e_i^{(\lambda)}(\vec p)\bar e_j^{(\lambda')}(\vec p\,')e_k^{(\lambda)}(\vec p)e_l^{(\lambda')}(\vec p\,')\frac{e^{i(\vec p+\vec p\,')\cdot\vec R}}{D_{\mathrm{i}}}\,, \tag{2.4}$$

where $\vec R=\vec R_B-\vec R_A$ and $D_{\mathrm{i}}=(p+k_B)(p+p')(p'-k_A+i\varepsilon)$. The polarization and angular sums are carried out using

$$\int\sum_{\lambda}e_i^{(\lambda)}(\vec p)\bar e_j^{(\lambda)}(\vec p)e^{\pm i\vec p\cdot\vec R}d\Omega=\frac{4\pi}{p^3}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{\sin pR}{R}\,. \tag{2.5}$$

We note that the relation (2.5) is employed in the calculation of all 12 contributions. Thus the total energy shift for a pair of randomly oriented molecules is the real part of

$$-\frac{(\hbar c)^3}{9\pi^2}|\mu(A)|^2|\mu(B)|^2(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}$$

$$\times\int_0^\infty\int_0^\infty \tfrac{1}{2}(\sin pR\,\sin p'\bar{R}+\sin p'R\,\sin p\bar{R})\sum_{\alpha=\mathrm{i}}^{\mathrm{xii}}\frac{1}{D_\alpha}dp\,dp' \ , \tag{2.6}$$

with $\bar{R}$ put equal to R after differentiation. From (2.1) it is clear that the principal value alone contributes to the integral for all diagrams except (x) and (xii). For these two diagrams we see from identity (2.2) that there is a real part, in addition to the principal-value contribution, arising from the δ-function products. It is given by

$$-\frac{1}{9\hbar c}|\mu(A)|^2|\mu(B)|^2(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}$$

$$\times\int_0^\infty\int_0^\infty \tfrac{1}{2}(\sin pR\,\sin p'\bar{R}+\sin p'R\,\sin p\bar{R})\left[\frac{1}{k_B-k_A}+\frac{1}{k_B+k_A}\right]\pi^2\delta(p-k_A)\delta(p'-k_A)dp\,dp'$$

$$=-\frac{1}{9\hbar c}|\mu(A)|^2|\mu(B)|^2(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}\frac{2k_B}{k_B^2-k_A^2}\sin k_AR\,\sin k_A\bar{R} \ . \tag{2.7}$$

To evaluate the principal-value integrals over p and p' in (2.6), we use the identity

$$\frac{\mathrm{P}}{x}\frac{\mathrm{P}}{y}=\frac{\mathrm{P}}{x-y}\left[\frac{\mathrm{P}}{y}-\frac{\mathrm{P}}{x}\right]+\pi^2\delta(x)\delta(y) \ . \tag{2.8}$$

The only graphs that give a nonzero δ-function product contribution for (2.8) are (x) and (xii) with $x=p-k_A$ and $y=p'-k_A$. In fact, this term is equal to that arising from (2.7), and the total energy therefore includes a contribution which is twice (2.7).

Finally, we use the identity (2.8) and determine the contribution arising from the resultant δ-function-independent part of the energy shift (2.6). The sums can be carried out in a manner similar to that for the ground-state case [10], leading to

$$-\frac{1}{9\pi^2\hbar c}|\mu(A)|^2|\mu(B)|^2(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}$$

$$\times\int_0^\infty\int_0^\infty \tfrac{1}{2}(\sin pR\,\sin p'\bar{R}+\sin p'R\,\sin p\bar{R})\frac{2(-k_A+k_B+p)}{(p-k_A)(p+k_B)(k_B-k_A)}\left[\frac{1}{p+p'}-\frac{1}{p-p'}\right]dp\,dp' \ , \tag{2.9}$$

which, on performing the p' integral, becomes

$$-\frac{1}{9\pi^2\hbar c}|\mu(A)|^2|\mu(B)|^2(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}$$

$$\times\frac{\pi}{(k_B-k_A)}\int_0^\infty\int_0^\infty \tfrac{1}{2}(\sin pR\,\sin p\bar{R}+\sin pR\,\sin p\bar{R})\frac{2(-k_A+k_B+p)}{(p-k_A)(p+k_B)(k_B-k_A)}dp \tag{2.10}$$

$$=-\frac{1}{9\pi\hbar c}|\mu(A)|^2|\mu(B)|^2(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}$$

$$\times\int_0^\infty\sin[p(R+\bar{R})]\left[\frac{1}{(k_B-k_A)(p-k_A)}+\frac{1}{(k_B-k_A)(p+k_B)}+\frac{1}{(k_B+k_A)(p-k_A)}+\frac{1}{(k_B+k_A)(p+k_B)}\right]dp \tag{2.11}$$

$$=-\frac{2}{9\pi\hbar c}\frac{|\mu(A)|^2|\mu(B)|^2}{(k_A^2-k_B^2)}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{\bar{R}}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}$$

$$\times\{-k_Af(k_B(R+\bar{R}))+k_Bf(k_A(R+\bar{R}))-\pi k_B\cos[k_A(R+\bar{R})]\} \tag{2.12}$$

where the final steps uses the principal-value integral [11]

$$\mathrm{P}\int_0^\infty\frac{\sin ax}{(x-b)}dx=-f(ab)+\pi\cos(ab),\ a,b>0 \ . \tag{2.13}$$

We remark that the energy shift from the f-dependent terms of (2.12) is the negative of the corresponding shift (2.14) for the pair of two-level molecules in their ground states. As may be seen from (1.6), the shift for a pair of two-level molecules in their ground states is

$$\begin{aligned} V_{GG}(R) = & -\frac{2}{9\pi\hbar c}\frac{|\mu(A)|^2|\mu(B)|^2}{(k_A^2-k_B^2)}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}} \\ & \times[k_A f(k_B(R+\bar{R}))-k_B f(k_A(R+\bar{R}))]\big|_{R=\bar{R}} \\ \equiv & \, \Phi(R) , \end{aligned} \tag{2.14}$$

where $\hbar c k_A$ and $\hbar c k_B$ are the energy spacings for A and B; $\Phi(R)$ has been introduced for use in the subsequent work.

The total energy shift for an excited molecule A and a ground-state molecule B is the sum of (2.12) and *twice* (2.7).

$$\begin{aligned} V_{EG}(R) = & -\Phi(R)+\frac{2k_B}{9\hbar c}\frac{|\mu(A)|^2|\mu(B)|^2}{(k_A^2-k_B^2)}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}} \\ & \times\{\cos[k_A(R+\bar{R})]+2\sin k_A R \sin k_A\bar{R}\}\Big|_{R=\bar{R}} . \end{aligned} \tag{2.15}$$

The trigonometric terms in (2.15) correspond to real-photon exchange. These simplify to the polynomial expression (2.16)

$$-\frac{4k_B}{9\hbar c}\frac{|\mu(A)|^2|\mu(B)|^2}{(k_B^2-k_A^2)}k_A^6\left[\frac{1}{k_A^2R^2}+\frac{1}{k_A^4R^4}+\frac{3}{k_A^6R^6}\right] . \tag{2.16}$$

Hence

$$V_{EG}(R)=-\Phi(R)-\frac{4k_B}{9\hbar c}\frac{|\mu(A)|^2|\mu(B)|^2}{(k_B^2-k_A^2)}k_A^6\left[\frac{1}{k_A^2R^2}+\frac{1}{k_A^4R^4}+\frac{3}{k_A^6R^6}\right] , \tag{2.17}$$

which, for multilevel systems, generalizes to the result (2.18), in agreement with the potential given in Ref. [8].

$$\begin{aligned} V_{EG}(R) = & -\frac{2}{3\pi}\sum_r\int_0^\infty\frac{k_{rm}|\mu^{mr}(A)|^2}{(k_{rm}^2+u^2)}\alpha^B(icu)u^6e^{-2uR}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right]du \\ & -\tfrac{2}{3}\sum_{\substack{r \\ E_r<E_m}}|\mu^{mr}(A)|^2\alpha^B(ck_{mr})k_{mr}^6\left[\frac{1}{k_{mr}^2R^2}+\frac{1}{k_{mr}^4R^4}+\frac{3}{k_{mr}^6R^6}\right] . \end{aligned} \tag{2.18}$$

We note that in the real-photon term, only downward transitions contribute. However, in the virtual-photon term, both upward and downward transitions from $|m\rangle$ contribute and the sum over r is unrestricted; the sign of the individual contribution is determined by that of k_{rm}.

It is instructive to examine the asymptotic limits of this energy shift. In the near zone, i.e., for small-R separations, the lead terms in both the real- and virtual-photon exchange contributions are proportional to R^{-6}. When *added* they give the result (1.8). On the other hand, for large R the real-photon contribution dominates and the resulting potential falls off as R^{-2}. It is given by

$$V_{EG}(R)=-\tfrac{2}{3}\sum_{\substack{r \\ E_r<E_m}}|\mu^{mr}(A)|^2\alpha^B(ck_{mr})\frac{k_{mr}^4}{R^2} , \tag{2.19}$$

where $\alpha^B(ck_{mr})$ is the polarizability of B at the transition frequency ck_{mr} of A.

The method is easily extended to the case of two electronically excited molecules and the result confirms the interaction potential found using response theory, and presented in Ref. [8].

III. A SPECIAL CASE: IDENTICAL MOLECULES

The explicit form of the Casimir-Polder potential as given by (1.7) cannot hold exactly when the molecules A and B have one or more common energy spacings, in particular for identical molecules. This is because the denominator vanishes when the spacings are equal. However, the multiplicative factor in (1.7) also vanishes under the same conditions and we therefore can obtain a modified expression for the potential. The essential features are easily seen from a consideration of two molecules under the two-level approximation. For this case the potential energy is given by (2.14), and for identical molecules we have

$$\lim_{k_B\to k_A(\equiv k_0)}\Phi(R)=-\frac{2}{9\pi\hbar c}|\mu|^4(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}$$

$$\times\lim_{k_B\to k_A(\equiv k_0)}\left.\frac{k_Af(k_B(R+\bar{R}))-k_Bf(k_A(R+\bar{R}))}{k_A^2-k_B^2}\right|_{\bar{R}=R}$$

$$=-\frac{2}{9\pi\hbar c}|\mu|^4(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^R\frac{1}{R}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)^{\bar{R}}\frac{1}{\bar{R}}$$

$$\times\left.\frac{f(k_0(R+\bar{R}))-k_0^2(R+\bar{R})g(k_0(R+\bar{R}))}{2k_0}\right|_{\bar{R}=R}, \tag{3.1}$$

where $\hbar ck_0$ is the common energy spacing. After carrying out the differentiations in (3.1) we obtain the explicit form (3.2) for the potential:

$$-\frac{2}{9\pi\hbar c}\frac{|\mu|^4k_0^3}{R^2}\left[-\frac{1}{k_0R}+\frac{6}{k_0^3R^3}-f(2k_0R)\left[-1+\frac{7}{k_0^2R^2}-\frac{3}{k_0^4R^4}\right]+g(2k_0R)\left[2k_0R-\frac{6}{k_0R}+\frac{6}{k_0^3R^3}\right]\right]. \tag{3.2}$$

The results for multilevel molecules follow in a straightforward manner. The complete interaction energy is given by (1.7) (where the summation excludes $k_{r0}=k_{s0}$) plus the r sum over terms (3.2) with $k_0=k_{r0}$ and $\mu=\mu^{r0}$.

A similar treatment can be made for two molecules in the same excited state. In the two-level approximation, the potential can be found from the appropriate limit. The limit of the virtual-photon term is, of course, (3.2), and the limit of the *two* terms associated with real photons is

$$-\frac{2}{9\hbar c}\frac{|\mu|^4k_0^3}{R^2}\left[3+\frac{1}{k_0^2R^2}-\frac{3}{k_0^4R^4}\right]. \tag{3.3}$$

As for a pair of ground-state molecules, the result for multilevel molecules in excited states may be obtained by generalizing the two-level model. Care must be taken in the multilevel case to include upward transitions from the excited state.

Finally, we point out that the limiting procedure used above does not apply to the calculation of the potential for two identical, two-level molecules when one is in the excited state and the other in the ground state. The limit $k_B\to k_A$ of (2.15) does not exist. That (1.11) does not apply may be seen from the graphs (iii), (iv), (ix), and (x) where the intermediate state $|\mathrm{II}\rangle$ is degenerate with the initial state. The degeneracy is lifted in lower order of perturbation. The resultant molecular stationary states are the superpositions

$$\Psi_\pm=\frac{1}{\sqrt{2}}\{|k_0,0\rangle\pm|0,k_0\rangle\}. \tag{3.4}$$

The energy shifts for these states are orientation dependent and vanish on random averaging.

IV. DISCUSSION

The dispersion energies for a pair of molecules (ground and excited), V_{GG} [Eq. (1.7)] and V_{EG} [Eq. (2.23)], derived in this paper agree with the results from our earlier work [8] based on response theory. However, for systems involving excited molecules they differ from the calculations of McLone and Power [5], Philpott [6], and Kweon and Lawandy [7], who employed fourth-order perturbation theory. The $\Phi(R)$ contributions in the potentials agree with those of the previous workers and the differences lie in the real-photon terms. The previous workers evaluated Eq. (1.11) using the principal value at every pole. As is seen from our present work, this is incomplete and the principal-value contribution must be supplemented by the δ-function product [see identity (2.2)]. A consequence of including this product is that (2.7) carries a weight of *two* in (2.15). The resultant energy shift due to real photons is a polynomial in $(1/k_AR)$ as given by (2.16). However, the corresponding shift in previous works [5–7,12] shows modulated behavior through trigonometrical factors such as $\sin k_AR$ and $\cos k_AR$. The explicit expression for (2.7) is

$$-\frac{4k_B}{9\hbar c}\frac{|\mu(A)|^2|\mu(B)|^2}{(k_B^2-k_A^2)}\frac{k_A^4}{R^2}\left\{\sin^2k_AR+\frac{2\sin k_AR\cos k_AR}{k_AR}+\frac{(3\cos^2k_AR-2\sin^2k_AR)}{k_A^2R^2}\right.$$

$$\left.-\frac{6\sin k_AR\cos k_AR}{k_A^3R^3}-\frac{3\sin^2k_AR}{k_A^4R^4}\right\}. \tag{4.1}$$

If this is added to the shift based on principal-value integrations, the resultant is *unmodulated* and is

$$-\frac{4k_B}{9\hbar c}\frac{|\mu(A)|^2|\mu(B)|^2}{(k_B^2-k_A^2)}k_A^6\left[\frac{1}{k_A^2R^2}+\frac{1}{k^4R^4}+\frac{3}{k_A^6R^6}\right] \tag{4.2}$$

in agreement with (2.16). These manipulations may be bypassed by using the identity

$$\mathrm{Re}\left[\frac{1}{x-i\varepsilon}\frac{1}{y+i\varepsilon}\right]=\frac{\mathrm{P}}{x-y}\left[\frac{\mathrm{P}}{y}-\frac{\mathrm{P}}{x}\right]+2\pi^2\delta(x)\delta(y)\ , \tag{4.3}$$

which follows from (2.2) and (2.8).

It is clear from (4.1) that this additional contribution to the shift does not affect the near-zone limiting form since the modulating factor of the R^{-6} term vanishes for small R. On the other hand, this correction is important for the far-zone potential and leads to the physically expected unmodulated R^{-2} behavior in the asymptotic limit of the complete potential. Similar arguments apply to the case of two excited molecules.

The textbook treatment [12] of interatomic interactions involving atoms in particular magnetic substates suffers from the neglect of these δ-function product terms. The potentials presented in [12] are modulated, but the inclusion of these δ-function terms leads to correct unmodulated results such as (4.6) and (4.7). It must be borne in mind that for excited atoms in magnetic substates, random orientation averaging is inappropriate. The modified result involving real photons for an excited atom A is

$$-\sum_{\substack{r\\E_r<E_m}}\mu_i^{mr}(A)\mu_j^{rm}(A)\alpha^B(ck_{mr})k_{mr}^6\left\{\frac{\alpha_{ik}\alpha_{jk}}{k_{mr}^2R^2}+\frac{\beta_{ik}\beta_{jk}-2\alpha_{ik}\beta_{jk}}{k_{mr}^2R^2}+\frac{\beta_{ik}\beta_{jk}}{k_{mr}^2R^2}\right\}, \tag{4.4}$$

where the tensors α_{ik} and β_{ik} are defined by

$$\alpha_{ik}=\delta_{ik}-\hat{R}_i\hat{R}_k,\quad \beta_{ik}=\delta_{ik}-3\hat{R}_i\hat{R}_k\ . \tag{4.5}$$

For the specific case where atom A is in one of the $2p_0, 2p_{\pm1}$ states, the far-zone interactions following from (2.18) are

$$V_{m=0}(R)\simeq-4|\mu(A)|^2\alpha^B(ck_A)\frac{k_A^2}{R^4}\ , \tag{4.6}$$

$$V_{m=\pm1}(R)\simeq-|\mu(A)|^2\alpha^B(ck_A)\frac{k_A^4}{R^2}\ , \tag{4.7}$$

where we have taken the intermolecular axis as the axis of quantization. It is to be noted that the R dependence for the $m=0$ case is R^{-4} whereas that for $m=\pm1$ is R^{-2}.

The computation of the van der Waals–Casimir interaction between two molecules in their ground states is an exact stationary-state problem. If one or both molecules are excited, the problem is not one involving precise stationary states because of the probability of decay. However, the concept of intermolecular energy shift is still a valid one provided the lifetimes for decay are sufficiently long compared with the light transit time R/c. For lifetimes typically of the order 10^{-8} s, it is physically meaningful to examine intermolecular potentials between molecules separated by hundreds of angstroms. The potentials computed in this paper fall into this category and can play an important role in phenomena involving excited chromophores separated by large distances within complex molecules.

ACKNOWLEDGMENT

E.A.P. thanks the Leverhulme Trust for support.

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