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Quantum electrodynamics with nonrelativistic sources. V. Electromagnetic field correlations and intermolecular interactions between molecules in either ground or excited states

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Spatial correlations between electromagnetic fields arising from neutral sources with electric-dipole transition moments are calculated using nonrelativistic quantum electrodynamics in the multipolar formalism. Expressions for electric-electric, magnetic-magnetic, and electric-magnetic correlation functions at two points **r** and **r**′ are given for a source molecule in either a ground or an excited state. In contrast to the electric-electric and magnetic-magnetic cases there are no electric-magnetic correlations for a ground-state molecule. For an excited molecule the downward transitions contribute additional terms which have modulating factors depending on $(r-r')/\lambda\!\!\!^-$. From these correlation functions electric and magnetic energy densities are found by setting $\mathbf{r}=\mathbf{r}'$. These energy densities are then used in a response formalism to calculate intermolecular energy shifts. In the case of two ground-state molecules this leads to the Casimir-Polder potential. However, for a pair of molecules, one or both excited, there are additional terms arising from downward transitions. An important feature of these energies is that they exhibit an R^{-2} dependence for large intermolecular separations R. This dependence is interpreted in terms of the Poynting vector, which itself can be obtained by setting $\mathbf{r}=\mathbf{r}'$ in the electric-magnetic correlation function.

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I. INTRODUCTION

The van der Waals interaction between two molecules in their ground states is well understood. However, if one or both molecules are excited, the concept of intermolecular energy is still a valid one provided the lifetimes for decay are sufficiently long compared with the light transit times R/c, where R is the intermolecular separation. For lifetimes typically of the order of 10^{-8} sec it is physically meaningful to examine intermolecular potentials between excited molecules separated by hundreds of angstroms. In the London limit it is well known that the interaction between two molecules in their ground states is attractive with an R^{-6} power law. When both molecules are excited the potential energy gives a repulsive force arising from downward transitions. If only one of the pair is excited the sign of the potential depends on the relative magnitudes of the relevant transition energies of the two molecules. In both cases the power law remains R^{-6} in the near zone, i.e., in the London limit of the fully retarded interaction. The explicit expressions for the near-zone potentials are given in [1]. The van der Waals potentials for large intermolecular separations differ from these because the finite speed of propagation begins to play an important role in the mechanism of interaction. The Casimir-Polder potential [2] is the predicted interaction energy when this retardation effect is fully taken into account. The complete potential shows a complicated dependence on R, tending to the R^{-6} power law when R is much less than the reduced wavelengths for dipole-allowed molecular transitions. For large separations the power law tends to R^{-7}. The complete theory of intermolecular interactions is based on quantum electrodynamics. Although the original formulation employed the minimal-coupling Hamiltonian, it is now common to use the multipolar form of the theory to study intermolecular effects and indeed all radiation-molecule interactions. The main advantage of multipolar quantum electrodynamics is that, except for the Coulomb binding within each molecule, all electromagnetic effects are characterized by transverse photon interactions, as, for example, their exchange leading to intermolecular forces. This, in addition to simplifying the detailed calculations, ensures that the causal requirements of physical phenomena are automatically satisfied.

In the present work we investigate the retarded intermolecular effects between molecules in either ground or excited states. As a prelude to this study we determine second-order correlations between the electromagnetic fields at two field points. Expectation values of electric-magnetic correlation in the limit of identical field points is immediately related to the Poynting vector and the result is in agreement with our previous work in this series [3] based on the Heisenberg formalism. Similarly the expectation values for both the electric-electric and magnetic-magnetic field-operator products at identical field points lead to known results for the energy densities in the vicinity of molecules in either ground or excited states. A manifestation of these energy densities is the energy shift produced on a test polarizable molecule in response to the electromagnetic fields. For two molecules in their ground states this approach leads to the dispersion force. When the source molecule is in an excited state the intermolecular energy shift has an unmodulated term including a part that falls off as R^{-2}. Previous work [4] on this shift provided only a partial determination valid for a limited range of R. In this paper we present a comprehensive analysis of the theory of intermolecular interactions and give expressions for the potential valid for all separations outside molecular overlap.

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II. BASIC THEORY AND SECOND-ORDER FIELD CORRELATIONS

In the multipolar formalism, which is used in this series, the momentum canonically conjugate to the vector potential $\mathbf{a}(\mathbf{r})$ is proportional to the transverse displacement-vector field $\mathbf{d}(\mathbf{r})$. In this formulation the electromagnetic gauge used is the Coulomb gauge and the sole longitudinal contributions are the intramolecular Coulomb binding potentials. For an electrically neutral source the *total* electric field is equal to the transverse Maxwell displacement vector outside the source since $\mathrm{div}\mathbf{d}=0$ [3(b),5]. Thus in calculations involving the total electric field one may use the displacement vector field. In this section we use the multipolar Hamiltonian in the electric-dipole approximation. The extension to higher moments and to magnetic effects is straightforward, but results in technically complicated expressions. The electric-dipole transition moment for molecular states $|m\rangle$ and $|n\rangle$ is written μ^{mn}. In this section we determine the expectation values of three spatial correlation functions of the electric and magnetic fields, namely $\langle d_i(\mathbf{r})b_j(\mathbf{r}')\rangle$, $\langle d_i(\mathbf{r})d_j(\mathbf{r}')\rangle$, and $\langle b_i(\mathbf{r})b_j(\mathbf{r}')\rangle$ for the electromagnetic vacuum and a molecule either in an excited state $|n\rangle$ or in its ground state $|0\rangle$. These expectation values are found to second order in the electric-dipole transition moments of the source molecule. In the Schrödinger picture, with the radiation-molecule interaction Hamiltonian

$$H_{\text{int}}=-\sum_{m,n}\mu^{mn}\cdot\mathbf{d}(0)|m\rangle\langle n| \,, \tag{2.1}$$

the second-order unnormalized wave function expressed in terms of the unperturbed states is

$$|n;0\rangle_{\text{pert}}=|n,0\rangle-\frac{1}{\hbar c}\sum_{\mathbf{p},m}|m;\mathbf{p}\rangle\frac{\langle\mathbf{p};m|H_{\text{int}}|n;0\rangle}{(p-k_{nm}-i\varepsilon)} +\frac{1}{(\hbar c)^2}\sum_{\substack{\mathbf{p},\mathbf{p}'\\ m,n'}}|n';\mathbf{p},\mathbf{p}'\rangle\frac{\langle\mathbf{p}',\mathbf{p};n'|H_{\text{int}}|m;\mathbf{p}\rangle\langle\mathbf{p};m|H_{\text{int}}|n;0\rangle}{(p-k_{nm}-i\varepsilon)(p+p'-k_{nn'}-i\varepsilon)} \,, \tag{2.2}$$

where $|m,p\rangle$ represents the bare state with molecule in state $|m\rangle$ and the field with a photon of wave vector $\mathbf{p}$ (the polarization character is implicit); the wave number k_{nm} is that associated with the $n\leftarrow m$ transition of the molecule, i.e., $k_{nm}=(E_n-E_m)/\hbar c$. In (2.2) the displacement of the poles shown by the addition of $-i\varepsilon$ is based on the adiabatic switching on of the interaction. We now calculate the various correlation functions using this wave function with the aid of the expansions for the displacement-vector field and the magnetic field in terms of the annihilation operators $a(\mathbf{p},\lambda)$ and the creation operators $a^\dagger(\mathbf{p},\lambda)$, namely

$$\mathbf{d}(\mathbf{r})=i\sum_{\mathbf{p},\lambda}\left[\frac{2\pi\hbar cp}{V}\right]^{1/2}[\mathbf{e}(\mathbf{p},\lambda)a(\mathbf{p},\lambda)e^{i\mathbf{p}\cdot\mathbf{r}} -\bar{\mathbf{e}}(\mathbf{p},\lambda)a^\dagger(\mathbf{p},\lambda)e^{-i\mathbf{p}\cdot\mathbf{r}}] \,,$$

$$\mathbf{b}(\mathbf{r})=i\sum_{\mathbf{p},\lambda}\left[\frac{2\pi\hbar cp}{V}\right]^{1/2}[\mathbf{b}(\mathbf{p},\lambda)a(\mathbf{p},\lambda)e^{i\mathbf{p}\cdot\mathbf{r}} -\bar{\mathbf{b}}(\mathbf{p},\lambda)a^\dagger(\mathbf{p},\lambda)e^{-i\mathbf{p}\cdot\mathbf{r}}] \,. \tag{2.3}$$

In (2.3) V is the quantization volume and $\mathbf{e}(\mathbf{p},\lambda)$ and $\mathbf{b}(\mathbf{p},\lambda)$ are the complex unit vectors defining the electric- and magnetic-field polarizations. From now on we suppress the explicit dependence of these vectors on $\mathbf{p}$ and λ.

A. The electric-magnetic correlation function

The correlation function between the electric and magnetic fields is

$$\begin{aligned}\langle d_i(\mathbf{r})b_j(\mathbf{r}')\rangle={}&\frac{1}{\hbar^2c^2}\sum_{\substack{m\\ \mathbf{p},\mathbf{p}'}}\frac{\langle 0;n|H_{\text{int}}|m;\mathbf{p}\rangle\langle\mathbf{p};m|d_i(\mathbf{r})b_j(\mathbf{r}')|m;\mathbf{p}'\rangle\langle\mathbf{p}';m|H_{\text{int}}|n;0\rangle}{(p-k_{nm}+i\varepsilon)(p'-k_{nm}-i\varepsilon)}\\ &+\frac{1}{\hbar^2c^2}\sum_{\substack{m\\ \mathbf{p},\mathbf{p}'}}\frac{\langle 0;n|d_i(\mathbf{r})b_j(\mathbf{r}')|n;\mathbf{p},\mathbf{p}'\rangle\langle\mathbf{p}',\mathbf{p};n|H_{\text{int}}|m;\mathbf{p}\rangle\langle\mathbf{p};m|H_{\text{int}}|n;0\rangle}{(p-k_{nm}-i\varepsilon)(p+p')}\\ &+\frac{1}{\hbar^2c^2}\sum_{\substack{m\\ \mathbf{p},\mathbf{p}'}}\frac{\langle 0;n|H_{\text{int}}|m;\mathbf{p}'\rangle\langle\mathbf{p}';m|H_{\text{int}}|n;\mathbf{p},\mathbf{p}'\rangle\langle\mathbf{p}'\mathbf{p};n|d_i(\mathbf{r})b_j(\mathbf{r}')|n;0\rangle}{(p'-k_{nm}+i\varepsilon)(p+p')} \,.\end{aligned} \tag{2.4}$$

The matrix elements of H_{int} and of $d_i(\mathbf{r})b_j(\mathbf{r}')$ are calculated using (2.3) and the polarization sums implicit in (2.4) are effected using

$$\begin{aligned}&\sum_{\text{pol}} e_i\bar{e}_j=\sum_{\text{pol}} b_i\bar{b}_j=(\delta_{ij}-\hat{p}_i\hat{p}_j)\;,\\&\sum_{\text{pol}} e_i\bar{b}_j=\varepsilon_{ijk}\hat{p}_k\;.\end{aligned}\tag{2.5}$$

The wave-vector sums are then converted into integrals using the continuum approximation. The resulting angular integrals can be evaluated using [6]

$$\tau_{ij}(pr)\equiv\int(\delta_{ij}-\hat{p}_i\hat{p}_j)e^{\pm i\mathbf{p}\cdot\mathbf{r}}\frac{d\Omega}{4\pi}=\left\{(\delta_{ij}-\hat{r}_i\hat{r}_j)\frac{\sin(pr)}{pr}+(\delta_{ij}-3\hat{r}_i\hat{r}_j)\left[\frac{\cos(pr)}{p^2r^2}-\frac{\sin(pr)}{p^3r^3}\right]\right\}\;,\tag{2.6}$$

$$\pm t_{ij}(pr)\equiv\varepsilon_{ijk}\int\hat{p}_k e^{\pm i\mathbf{p}\cdot\mathbf{r}}\frac{d\Omega}{4\pi}=\mp i\varepsilon_{ijk}\left[\frac{\cos(pr)}{pr}-\frac{\sin(pr)}{p^2r^2}\right]\hat{r}_k\;.\tag{2.7}$$

The correlation function (2.4) can then be written as

$$\begin{aligned}\frac{1}{\pi^2}\sum_m\mu_k^{nm}\mu_l^{mn}\int\int dp\,dp'p^3p'^3&\left\{\frac{\tau_{ik}(pr)t_{lj}(p'r')-t_{kj}(pr')\tau_{li}(p'r)}{(p-k_{nm}+i\varepsilon)(p'-k_{nm}-i\varepsilon)}\right.\\&\left.+\frac{\tau_{il}(pr)t_{kj}(p'r')+t_{lj}(pr')\tau_{ik}(p'r)}{(p-k_{nm}-i\varepsilon)(p+p')}-\frac{t_{il}(pr)t_{kj}(p'r')+t_{lj}(pr')\tau_{ik}(p'r)}{(p'-k_{nm}+i\varepsilon)(p+p')}\right\}\;.\end{aligned}\tag{2.8}$$

For nondegenerate states $|n\rangle$ and $|m\rangle$ the transition moment $\boldsymbol{\mu}^{mn}$ can be chosen real so that $\mu_k^{nm}\mu_l^{mn}$ is k-l symmetric. Using this fact together with judicious changes in the integration variables the correlation function (2.8) can be written as

$$\begin{aligned}\langle d_i(\mathbf{r})b_j(\mathbf{r}')\rangle=\frac{1}{\pi^2}\sum_m\mu_k^{nm}\mu_l^{mn}\int_0^\infty\int_0^\infty dp\,dp'p^3p'^3\tau_{ik}(pr)t_{lj}(p'r')&\\\times\left\{\frac{1}{(p-k_{nm}-i\varepsilon)}\left[\frac{1}{p+p'}-\frac{1}{p'-p+2i\varepsilon}\right]\right.&\\\left.-\frac{1}{(p'-k_{nm}+i\varepsilon)}\left[\frac{1}{p+p'}-\frac{1}{p'-p+2i\varepsilon}\right]-\text{c.c.}\right\}\;.&\end{aligned}\tag{2.9}$$

To perform the integrations in (2.9) we use the distribution identity

$$\frac{1}{x-x_0\pm i\varepsilon}=\mathrm{P}\frac{1}{x-x_0}\mp i\pi\delta(x-x_0)\;,\tag{2.10}$$

where P denotes principal value, for the four denominators. First we note that the terms involving $i\pi\delta(p-p')$ mutually cancel. Second, when the integration limits applied to x in (2.10) are $(0,\infty)$ the δ function contributes only for $x_0>0$. Thus in (2.9) we need to distinguish upward from downward transitions corresponding to k_{nm} being negative or positive. We find that the contribution to the expectation value of this correlation function is zero for upward transitions from $|n\rangle$. The downward transitions contribute to this expectation value and we have

$$\begin{aligned}\langle d_i(\mathbf{r})b_j(\mathbf{r}')\rangle&=\frac{2i}{\pi}\sum_{\substack{m\\E_m<E_n}}\mu_k^{nm}\mu_l^{mn}\int_0^\infty\int_0^\infty dp\,dp'p^3p'^3\tau_{ik}(pr)t_{lj}(p'r')\left[\frac{1}{p+p'}-\frac{PV}{p'-p}\right][\delta(p-k_{nm})+\delta(p'-k_{nm})]\\&=\frac{2i}{\pi}\sum_{\substack{m\\E_m<E_n}}k_{nm}^3\mu_k^{nm}\mu_l^{mn}\left\{\tau_{ik}(k_{nm}r)\mathrm{P}\int_{-\infty}^\infty dp'p'^3\frac{t_{lj}(p'r')}{p'+k_{nm}}+t_{lj}(k_{nm}r')\mathrm{P}\int_{-\infty}^\infty dp\,p^3\frac{\tau_{ik}(pr)}{p+k_{nm}}\right\}\;.\end{aligned}\tag{2.11}$$

The integrals in (2.11) can be expressed in terms of elementary functions. We define the functions σ_{ij} and s_{ij} conjugate to τ_{ij} (2.6) and t_{ij} (2.7) by

$$\sigma_{ij}(pr)=(\delta_{ij}-\hat{r}_i\hat{r}_j)\frac{\cos(pr)}{pr}-(\delta_{ij}-3\hat{r}_i\hat{r}_j)\left[\frac{\sin(pr)}{p^2r^2}+\frac{\cos(pr)}{p^3r^3}\right]\;,\tag{2.12}$$

$$s_{ij}(pr)=-i\varepsilon_{ijk}\hat{r}_k\left[\frac{\sin(pr)}{pr}+\frac{\cos(pr)}{p^2r^2}\right]\;.\tag{2.13}$$

Then the electric-magnetic correlation function is

$$\langle d_i(\mathbf{r})b_j(\mathbf{r}')\rangle = 2i \sum_{\substack{m \\ E_m<E_n}} k_{nm}^6 \mu_k^{nm}\mu_l^{mn}[\tau_{ik}(k_{nm}r)s_{lj}(k_{nm}r')+t_{lj}(k_{nm}r')\sigma_{ik}(k_{nm}r)] \tag{2.14}$$

$$= -\frac{2\varepsilon_{jlm}\hat{r}'_m}{rr'} \sum_{\substack{m \\ E_m<E_n}} k_{nm}^4 \mu_k^{nm}\mu_l^{mn} \left\{ \cos[k_{nm}(r-r')] \left[\alpha_{ik} + \beta_{ik} \left[\frac{1}{k_{nm}^2 rr'} - \frac{1}{k_{nm}^2 r^2} \right] \right] \right.$$
$$\left. + \sin[k_{nm}(r-r')] \left[\frac{\alpha_{ik}}{k_{nm}r'} - \beta_{ik} \left[\frac{1}{k_{nm}r} + \frac{1}{k_{nm}^3 r^2 r'} \right] \right] \right\} . \tag{2.15}$$

We note that upward transitions do not contribute to this correlation function. As will be shown later, this is in direct contrast to the electric-electric and magnetic-magnetic correlation functions. For $\mathbf{r}=\mathbf{r}'$ expression (2.15) reduces to

$$\langle d_i(\mathbf{r})b_j(\mathbf{r})\rangle = -2\varepsilon_{jlm}\frac{(\delta_{ik}-\hat{r}_i\hat{r}_k)\hat{r}_n}{r^2} \sum_{\substack{m \\ E_m<E_n}} k_{nm}^4 \mu_k^{nm}\mu_l^{mn} , \tag{2.16}$$

which shows an inverse square dependence on r. From this result we can obtain the expectation value of the Poynting vector $\mathbf{S}$ by contracting (2.16) with $(c/4\pi)\varepsilon_{ijk}$. This yields

$$\mathbf{S}(\mathbf{r}) = \frac{c\hat{\mathbf{r}}}{2\pi r^2} \sum_{\substack{m \\ E_m<E_n}} k_{nm}^4 (\boldsymbol{\mu}^{nm}\cdot\boldsymbol{\mu}^{mn} - \boldsymbol{\mu}^{nm}\cdot\hat{\mathbf{r}}\boldsymbol{\mu}^{mn}\cdot\hat{\mathbf{r}}) \tag{2.17}$$

as expected [3(b),3(d)].

B. The electric-electric correlation function and energy density

The electric-electric spatial correlation expectation value for the state (2.2) can be written in a form similar to (2.9). We have

$$\langle d_i(\mathbf{r})d_j(\mathbf{r}')\rangle = \frac{1}{\pi^2}\sum_m \mu_k^{nm}\mu_l^{mn}\int_0^\infty\int_0^\infty dp\, dp' p^3 p'^3 \tau_{ik}(pr)\tau_{lj}(p'r')$$
$$\times \left\{ \frac{1}{(p-k_{nm}-i\varepsilon)} \left[\frac{1}{(p+p')} + \frac{1}{(p'-p+2i\varepsilon)} \right] \right.$$
$$\left. + \frac{1}{(p'-k_{nm}+i\varepsilon)} \left[\frac{1}{(p+p')} - \frac{1}{(p'-p+2i\varepsilon)} \right] + \text{c.c.} \right\} . \tag{2.18}$$

To proceed further we use Eq. (2.10) as before; however, those terms involving $i\pi\delta(p-p')$ do not cancel in the present case. They are

$$\frac{i}{\pi}\sum_m \mu_k^{nm}\mu_l^{mn}\int_0^\infty dp\, p^6 \tau_{ik}(pr)\tau_{lj}(pr') \left\{ \frac{1}{(p-k_{nm}+i\varepsilon)} - \frac{1}{(p-k_{nm}-i\varepsilon)} \right\} + \text{c.c.} \tag{2.19}$$

$$= 4 \sum_{E_m<E_n} \mu_k^{nm}\mu_l^{mn} k_{nm}^6 \tau_{ik}(k_{nm}r)\tau_{lj}(k_{nm}r') . \tag{2.20}$$

The remaining contribution to this correlation function is

$$\frac{2}{\pi^2}\sum_m \mu_k^{nm}\mu_l^{mn}\int_0^\infty\int_0^\infty dp\, dp' p^3 p'^3 \tau_{ik}(pr)\tau_{lj}(p'r') \left\{ \left[\frac{1}{(p+p')} + \frac{PV}{(p-p')} \right] \frac{PV}{(p-k_{nm})} \right.$$
$$\left. + \left[\frac{1}{(p+p')} - \frac{PV}{(p-p')} \right] \frac{PV}{(p'-k_{nm})} \right\} . \tag{2.21}$$

Using [6]

$$\int_{-\infty}^\infty dp' p'^3 \frac{\tau_{ij}(p'r)}{(p+p')} = \pi p^3 \sigma_{ij}(pr) \tag{2.22}$$

with $\sigma_{ij}(pr)$ given by (2.12), expression (2.21) is found to be

$$\frac{2}{\pi}\sum_m \mu_k^{nm}\mu_l^{mn}$$
$$\times \mathrm{P}\int_0^\infty dp \frac{p^6}{(p-k_{nm})}[\tau_{ik}(pr)\sigma_{lj}(pr')+\sigma_{ik}(pr)\tau_{lj}(pr')] . \tag{2.23}$$

In contrast to the $\langle d(\mathbf{r})b(\mathbf{r}')\rangle$ correlation discussed in Sec. II A we now have nonzero contributions from upward transitions.

1. Upward transitions

First we take the special case of $|n\rangle$ being the ground state $|0\rangle$ to evaluate (2.23) for one upward transition $|0\rangle\rightarrow|m\rangle$. Since $k_{m0}\equiv k_0>0$, there is no pole in the integrand in this case. The contribution to (2.23) is

$$\frac{2}{\pi}\mu_k^{0m}\mu_l^{m0}\int_0^\infty dp\frac{p^6}{(p+k_0)}[\tau_{ik}(pr)\sigma_{lj}(pr')+\sigma_{ik}(pr)\tau_{lj}(pr')]$$

$$=\frac{2}{\pi}\mu_k^{0m}\mu_l^{m0}\int_0^\infty dp\frac{p^4}{p+k_0}\left[\alpha_{ik}\alpha'_{lj}\sin[p(r+r')]-\alpha_{ik}\beta'_{lj}\frac{\cos[p(r+r')]}{pr'}+\beta_{ik}\alpha'_{lj}\frac{\cos[p(r+r')]}{pr}\right.$$
$$-\alpha_{ik}\beta'_{lj}\frac{\sin[p(r+r')]}{p^2r'^2}-\beta_{ik}\alpha'_{lj}\frac{\sin[p(r+r')]}{p^2r^2}-\beta_{ik}\beta'_{lj}\frac{\sin[p(r+r')]}{p^2rr'}$$
$$\left.-\beta_{ik}\beta'_{lj}\frac{\cos[p(r+r')]}{p^3rr'^2}-\beta_{ij}\beta'_{lj}\frac{\cos[p(r+r')]}{p^3r^2r'}+\beta_{ik}\beta'_{lj}\sin\frac{[p(r+r')}{p^4r^2r'^2}\right], \tag{2.24}$$

where we have used (2.6) and (2.12) for the tensors τ and σ. The p integration is effected using sine and cosine integrals and the combinations [7]

$$f(x)=\text{ci}(x)\sin x-\text{si}(x)\cos x=\int_0^\infty\frac{e^{-xu}}{1+u^2}du\ ,$$
$$g(x)=-\text{ci}(x)\cos x-\text{si}(x)\sin x=\int_0^\infty\frac{ue^{-xu}}{1+u^2}du\ , \tag{2.25}$$

and we obtain

$$\langle 0|d_i(\mathbf{r})d_j(\mathbf{r}')\rangle|0\rangle=\sum_m\langle d_i(\mathbf{r})d_j(\mathbf{r}')\rangle_{m\leftarrow 0}\ ,$$

where

$$\langle d_i(\mathbf{r})d_j(\mathbf{r}')\rangle_{m\leftarrow 0}=\frac{2k_0^4}{\pi}\mu_k^{0m}\mu_l^{m0}\frac{1}{rr'}\left\{\alpha_{ik}\alpha'_{lj}\left[\frac{2}{k_0^3(r+r')^3}-\frac{1}{k_0(r+r')}+f(k_0(r+r'))\right]\right.$$
$$+\frac{\alpha_{ik}\beta'_{lj}}{k_0r'}\left[\frac{1}{k_0^2(r+r')^2}-g(k_0(r+r'))\right]+\frac{\beta_{ik}\alpha'_{lj}}{k_0r}\left[\frac{1}{k_0^2(r+r')^2}-g(k_0(r+r'))\right]$$
$$+\frac{\alpha_{ik}\beta'_{lj}}{k_0^2r'^2}\left[\frac{1}{k_0(r+r')}-f(k_0(r+r'))\right]+\frac{\beta_{ij}\alpha'_{lj}}{k_0^2r^2}\left[\frac{1}{k_0(r+r')}-f(k_0(r+r'))\right]$$
$$+\frac{\beta_{ik}\beta'_{lj}}{k_0^2rr'}\left[\frac{1}{k_0(r+r')}-f(k_0(r+r'))\right]+\frac{\beta_{ik}\beta'_{lj}}{k_0^3rr'^2}[g(k_0(r+r'))]$$
$$\left.+\frac{\beta_{ik}\beta'_{lj}}{k_0^3r^2r'}[g(k_0(r+r'))]+\frac{\beta_{ik}\beta'_{lj}}{k_0^4r^2r'^2}[f(k_0(r+r'))]\right\}, \tag{2.26}$$

where $k_0=k_{m0}>0$, and $\langle\ \rangle_{m\leftarrow 0}$ denotes the contribution to the expectation value from the transition $m\leftarrow 0$. For identical field points, i.e., $\mathbf{r}=\mathbf{r}'$, we can use i,j and k,l symmetry to determine

$$\langle d_i(\mathbf{r})d_j(\mathbf{r})\rangle_{m\leftarrow 0}=\frac{2k_0^4}{\pi}\mu_k^{0m}\mu_l^{m0}\frac{1}{r^2}\left\{\alpha_{ik}\alpha_{lj}\left[\frac{1}{4k_0^3r^3}-\frac{1}{2k_0r}+f(2k_0r)\right]\right.$$
$$+\alpha_{ik}\beta_{lj}\left[\frac{3}{2k_0^3r^3}-\frac{2g(2k_0r)}{k_0r}-\frac{2f(2k_0r)}{k_0^2r^2}\right]$$
$$\left.+\beta_{ik}\beta_{lj}\left[\frac{1}{2k_0^3r^3}-\frac{f(2k_0r)}{k_0^2r^2}-\frac{2g(2k_0r)}{k_0^3r^3}+\frac{f(2k_0r)}{k_0^4r^4}\right]\right\}. \tag{2.27}$$

The asymptotic limits after spatial averaging of the molecular orientation are

$$\langle d_i(\mathbf{r})d_j(\mathbf{r})\rangle_{m\leftarrow 0}\simeq\begin{cases}\dfrac{|\boldsymbol{\mu}|^2}{6\pi k_0 r^7}(13\delta_{ij}+7\hat{r}_i\hat{r}_j), & k_0r\gg 1\\[2ex] \dfrac{|\boldsymbol{\mu}|^2}{3r^6}(\delta_{ij}+3\hat{r}_i\hat{r}_j), & k_0r\ll 1\ .\end{cases}\tag{2.28}$$

The electric energy density associated with the transition $m\leftarrow 0$ for an isotropic source follows from (2.27) and is

$$\frac{1}{8\pi}\langle d^2(\mathbf{r})\rangle_{m\leftarrow 0}=\frac{1}{12\pi^2}\frac{|\boldsymbol{\mu}^{m0}|^2}{r^2}k_0^4\left\{\frac{13}{2k_0^3r^3}-\frac{1}{k_0r}-f(2k_0r)\left[-2+\frac{10}{k_0^2r^2}+\frac{6}{k_0^4r^4}\right]-g(2k_0r)\left[\frac{4}{k_0r}-\frac{12}{k_0^3r^3}\right]\right\}\ .\tag{2.29}$$

This expression is equivalent to our previous result [3(d)] where the energy density was given as an integral (2.30) over a parameter u,

$$\frac{1}{6\pi^2}\int_0^\infty du\, u^6e^{-2ur}\frac{k_0|\boldsymbol{\mu}^{m0}|^2}{k_0^2+u^2}\left[\frac{1}{u^2r^2}+\frac{2}{u^3r^3}+\frac{5}{u^4r^4}+\frac{6}{u^5r^5}+\frac{3}{u^6r^6}\right]\ .\tag{2.30}$$

The above expressions are easily adapted to a general upward transition $m\leftarrow n$ with $k_{nm}<0$.

2. *Downward transitions*

From the expressions (2.20) and (2.23) for the total electric-electric correlation function we now extract the contributions arising from downward transitions. For simplicity we consider the transition $0\leftarrow p$ with $k_{p0}\equiv p_0>0$. The term from (2.20) for this transition is

$$4\mu_k^{p0}\mu_l^{0p}p_0^6\tau_{ik}(p_0r)\tau_{lj}(p_0r')=2\frac{\mu_k^{p0}\mu_l^{0p}p_0^4}{rr'}\left\{\cos[p_0(r-r')]\left[\alpha_{ik}\alpha'_{lj}-\frac{\alpha_{ik}\beta'_{lj}}{p_0^2r'^2}-\frac{\beta_{ik}\alpha'_{lj}}{p_0^2r^2}+\frac{\beta_{ik}\beta'_{lj}}{p_0^2rr'}+\frac{\beta_{ik}\beta'_{lj}}{p_0^4r^2r'^2}\right]\right.\tag{2.31}$$

$$+\sin[p_0(r-r')]\left[\frac{\alpha_{ik}\beta'_{lj}}{p_0r'}-\frac{\beta_{ik}\alpha'_{lj}}{p_0r}+\frac{\beta_{ik}\beta'_{lj}}{p_0^3rr'^2}-\frac{\beta_{ik}\beta'_{lj}}{p_0^3r^2r'}\right]$$

$$+\cos[p_0(r+r')]\left[-\alpha_{ik}\alpha'_{lj}+\frac{\alpha_{ik}\beta'_{lj}}{p_0^2r'^2}+\frac{\beta_{ik}\alpha'_{lj}}{p_0^2r^2}+\frac{\beta_{ik}\beta'_{lj}}{p_0^2rr'}-\frac{\beta_{ik}\beta'_{lj}}{p_0^4r^2r'^2}\right]$$

$$\left.+\sin[p_0(r+r')]\left[\frac{\alpha_{ik}\beta'_{lj}}{p_0r'}+\frac{\beta_{ik}\alpha'_{lj}}{p_0r}-\frac{\beta_{ik}\beta'_{lj}}{p_0^3rr'^2}-\frac{\beta_{ik}\beta'_{lj}}{p_0^3r^2r'}\right]\right\}\ .\tag{2.32}$$

The corresponding term arising from (2.23) is

$$\frac{2}{\pi}\mu_k^{p0}\mu_l^{0p}\mathbf{P}\int_0^\infty dp\frac{p^6}{(p-p_0)}[\tau_{ik}(pr)\sigma_{lj}(pr')+\sigma_{ik}(pr)\tau_{lj}(pr')]\tag{2.33}$$

$$=-\langle d_i(\mathbf{r})d_j(\mathbf{r}')\rangle_{p\leftarrow 0}+2\frac{\mu_k^{p0}\mu_l^{0p}p_0^4}{rr'}\left\{\cos[p_0(r+r')]\left[\alpha_{ik}\alpha'_{lj}-\frac{\alpha_{ik}\beta'_{lj}}{p_0^2r'^2}-\frac{\beta_{ik}\alpha'_{lj}}{p_0^2r^2}-\frac{\beta_{ik}\beta'_{lj}}{p_0^2rr'}+\frac{\beta_{ik}\beta'_{lj}}{p_0^4r^2r'^2}\right]\right.$$

$$\left.+\sin[p_0(r+r')]\left[-\frac{\alpha_{ik}\beta'_{lj}}{p_0r'}-\frac{\beta_{ik}\alpha'_{lj}}{p_0r}+\frac{\beta_{ik}\beta'_{lj}}{p_0^3rr'^2}+\frac{\beta_{ik}\beta'_{lj}}{p_0^3r^2r'}\right]\right\}\ ,\tag{2.34}$$

where $\langle d_i(\mathbf{r})d_j(\mathbf{r})\rangle_{p\leftarrow 0}$ is given by (2.26) with k_0 replaced by p_0. When (2.32) and (2.34) are summed to obtain the total contribution to the expectation value from the downward transition $0\leftarrow p$, the terms depending on $\cos p_0(r+r')$ and $\sin p_0(r+r')$ cancel. We have

$$\langle d_i(\mathbf{r})d_j(\mathbf{r})\rangle_{0\leftarrow p}=-\langle d_i(\mathbf{r})d_j(\mathbf{r}')\rangle_{p\leftarrow 0}+2\frac{\mu_k^{p0}\mu_l^{0p}p_0^4}{rr'}\left\{\cos[p_0(r-r')]\left[\alpha_{ik}\alpha'_{lj}-\frac{\alpha_{ik}\beta'_{lj}}{p_0^2r'^2}-\frac{\beta_{ik}\alpha'_{lj}}{p_0^2r^2}+\frac{\beta_{ik}\beta'_{lj}}{p_0^2rr'}+\frac{\beta_{ik}\beta'_{lj}}{p_0^4r^2r'^2}\right]\right.$$

$$\left.+\sin[p_0(r-r')]\left[\frac{\alpha_{ik}\beta'_{lj}}{p_0r'}-\frac{\beta_{ik}\alpha'_{lj}}{p_0r}+\frac{\beta_{ik}\beta'_{lj}}{p_0^3rr'^2}-\frac{\beta_{ik}\beta'_{lj}}{p_0^3r^2r'}\right]\right\}$$

$$(p_0=k_{p0}>0)\ .\tag{2.35}$$

A significant feature differentiating the contributions to the correlation function from upward and downward transitions is the presence, for downward transitions, of oscillatory terms due to real-photon emission and reabsorption. These terms depend on the radial difference $(r-r')$ with characteristic reduced wavelength $(1/p_0)$.

For identical field points

$$\langle d_i(\mathbf{r})d_j(\mathbf{r})\rangle_{0\leftarrow p}=-\langle d_i(\mathbf{r})d_j(\mathbf{r})\rangle_{p\leftarrow 0}+2\frac{\mu_k^{p0}\mu_l^{0p}p_0^4}{r^2}\left\{\alpha_{ik}\alpha_{lj}-2\frac{\alpha_{ik}\beta_{lj}}{p_0^2r^2}+\frac{\beta_{ik}\beta_{lj}}{p_0^2r^2}+\frac{\beta_{ik}\beta_{lj}}{p_0^4r^4}\right\}, \tag{2.36}$$

where $\langle d_i(\mathbf{r})d_j(\mathbf{r})\rangle_{p\leftarrow 0}$ is given by (2.27) with k_0 replaced by p_0. For an isotropic source

$$\langle d_i(\mathbf{r})d_j(\mathbf{r})\rangle_{0\leftarrow p}\simeq\begin{cases}\dfrac{2p_0^4|\boldsymbol{\mu}^{0p}|^2}{3r^2}(\delta_{ij}-\hat{r}_i\hat{r}_j), & p_0r\gg 1 \quad (2.37)\\[2ex] \dfrac{|\boldsymbol{\mu}^{0p}|^2}{3r^6}(\delta_{ij}+3\hat{r}_i\hat{r}_j), & p_0r\ll 1\ . \quad (2.38)\end{cases}$$

It is important to note the striking difference in the far-zone behavior of (2.37) and the ground-state expression (2.28). The r^{-2} dependence arises from the real photon emission in the present case. The r^{-7}-term due to virtual-photon exchange is still present, but is dominated by the real-photon-emission contribution. On the other hand, the near-zone expressions (2.28) and (2.38) are identical. This occurs since the r^{-6} contribution from virtual photons is the negative of (2.29) and the pole contribution in (2.36) is twice (2.29). The electric energy density associated with a downward transition $0\leftarrow p$ is found from (2.36). We have, for an isotropic source,

$$\frac{1}{8\pi}\langle\mathbf{d}^2(\mathbf{r})\rangle_{0\leftarrow p}=\frac{1}{12\pi^2}\frac{|\boldsymbol{\mu}^{p0}|^2p_0^4}{r^2}\left\{-\frac{13}{2p_0^3r^3}+\frac{1}{p_0r}+f(2p_0r)\left[-2+\frac{10}{p_0^2r^2}-\frac{6}{p_0^4r^4}\right]+g(2p_0r)\left[\frac{4}{p_0r}-\frac{12}{p_0^3r^3}\right]+\pi\left[2+\frac{2}{p_0^2r^2}+\frac{6}{p_0^4r^4}\right]\right\}. \tag{2.39}$$

It is instructive to compare the additional terms in (2.39) arising from real transition, namely

$$\frac{1}{6\pi}\frac{|\boldsymbol{\mu}^{0p}|^2}{r^6}(3+p_0^2r^2+p_0^4r^4) \tag{2.40}$$

with the electric energy density of a classical dipole source. The latter is

$$\frac{1}{8\pi}\mathbf{E}^2=\frac{1}{8\pi}\left\{\mathrm{Re}\mu_j^{\mathrm{class}}(-\nabla^2\delta_{ij}+\nabla_i\nabla_j)\frac{e^{i(p_0r-\omega t)}}{r}\right\}\times\left\{\mathrm{Re}\mu_k^{\mathrm{class}}(-\nabla^2\delta_{ik}+\nabla_i\nabla_k)\frac{e^{i(p_0r-\omega t)}}{r}\right\}, \tag{2.41}$$

which after orientation and cycle averaging becomes

$$\left\langle\frac{1}{8\pi}\mathbf{E}^2\right\rangle=\frac{|\boldsymbol{\mu}^{\mathrm{class}}|^2}{24\pi r^6}(3+p_0^2r^2+p_0^4r^4)\ . \tag{2.42}$$

The two expressions (2.40) and (2.42) are reconciled by the correspondence principle [8]

$$\boldsymbol{\mu}^{\mathrm{class}}=2\,\mathrm{Re}\langle|\boldsymbol{\mu}^{0p}|\rangle\ . \tag{2.43}$$

C. The magnetic-magnetic correlation function and energy density

The magnetic-magnetic correlation function for an electric-dipole source $\boldsymbol{\mu}$ can be expressed in a form analogous to (2.18). We consider the case of a downward transition with $p_0\equiv k_{p0}>0$:

$$\langle b_i(\mathbf{r})b_j(\mathbf{r}')\rangle_{0\leftarrow p}=\frac{1}{\pi^2}\mu_k^{p0}\mu_l^{0p}\int_0^\infty\int_0^\infty dp\,dp'p^3p'^3t_{ki}(pr)t_{lj}(p'r')\times\left\{\frac{1}{(p-p_0-i\varepsilon)}\left[\frac{1}{(p+p')}-\frac{1}{(p'-p+2i\varepsilon)}\right]+\frac{1}{(p-p_0+i\varepsilon)}\left[\frac{1}{(p+p')}+\frac{1}{(p'-p+2i\varepsilon)}\right]+\mathrm{c.c.}\right\}, \tag{2.44}$$

where t_{ij} is defined by (2.7). The calculation follows essentially the same steps as for the electric case in Sec. II B. We find

$$\langle b_i(\mathbf{r})b_j(\mathbf{r}')\rangle_{0\leftarrow p} = -\frac{2}{\pi r r'}\mu_k^{p0}\mu_l^{0p}\varepsilon_{ljm}\varepsilon_{kin}\hat{r}_n\hat{r}'_m \left\{ -\frac{2p_0}{(r+r')^3} + \frac{p_0^3}{(r+r')} - p_0^4 f(p_0(r+r')) - \left[\frac{1}{r}+\frac{1}{r'}\right]\frac{p_0}{(r+r')^2} + \left[\frac{1}{r}+\frac{1}{r'}\right]p_0^3 g(p_0(r+r')) - \frac{p_0}{rr'(r+r')} + \frac{p_0^3}{rr'}f(p_0(r+r')) - \pi p_0^4\cos[p_0(r-r')] - \pi p_0^3\left[\frac{1}{r'}-\frac{1}{r}\right]\sin[p_0(r-r')] - \pi\frac{p_0^2}{rr'}\cos[p_0(r-r')] \right\} . \tag{2.45}$$

We note, in passing, that the corresponding correlation function for upward transitions excludes the trigonometric terms in (2.45) and is the negative of the remaining terms.

For $\mathbf{r}=\mathbf{r}'$, we have

$$\langle b_i(\mathbf{r})b_j(\mathbf{r})\rangle_{0\leftarrow p} = -\frac{2}{\pi}\mu_k^{p0}\mu_l^{0p}\varepsilon_{ljm}\varepsilon_{kin}\frac{\hat{r}_n\hat{r}_m}{r} \times \left\{ -\frac{5p_0}{4r^3} + \frac{p_0^3}{2r} - p_0^4 f(2p_0 r) + \frac{2p_0^3}{r}g(2p_0 r) + \frac{p_0^2}{r^2}f(2p_0 r) - \pi p_0^4\left[1+\frac{1}{p_0^2 r^2}\right] \right\} . \tag{2.46}$$

For an isotropic source the asymptotic expressions of (2.46) are

$$\langle b_i(\mathbf{r})b_j(\mathbf{r})\rangle_{0\leftarrow p} \simeq \begin{cases} \dfrac{2p_0^4|\mu^{0p}|^2}{3r^2}(\delta_{ij}-\hat{r}_i\hat{r}_j), & p_0 r \gg 1 \quad (2.47) \\ \dfrac{5}{6\pi}\dfrac{|\mu^{0p}|^2 p_0}{r^5}(\delta_{ij}-\hat{r}_i\hat{r}_j), & p_0 r \ll 1 . \end{cases} \tag{2.48}$$

The far-zone expression is, as expected, the same as (2.37). The near-zone result is different from its electric analog (2.38) in that it depends on p_0 and the power law is r^{-5} instead of r^{-6}.

It is straightforward to use these results to find the magnetic energy density due to an electric-dipole source. For an isotropic source

$$\frac{1}{8\pi}\langle b^2(\mathbf{r})\rangle_{0\leftarrow p} = -\frac{1}{6\pi^2}\frac{|\mu^{0p}|^2}{r^2} \times p_0^4\left\{ -\frac{5}{4r^3} + \frac{1}{2p_0 r} - f(2p_0 r) + \frac{2}{p_0 r}g(2p_0 r) + \frac{1}{p_0^2 r^2}f(2p_0 r) - \pi\left[1+\frac{1}{p_0^2 r^2}\right] \right\} . \tag{2.49}$$

As previously noted a correlation function for an upward transition may be found from the negative of (2.45) by replacing p_0 by k_0 and excluding the trigonometric terms. The integral form for this energy density [cf. (2.30)] is

$$-\frac{1}{6\pi^2}\int_0^\infty du\, u^6 e^{-2ur}\frac{k_0|\mu^{m0}|^2}{k_0^2+u^2}\left[\frac{1}{u^2r^2}+\frac{2}{u^3r^3}+\frac{1}{u^4r^4}\right] . \tag{2.50}$$

Finally, we quote the asymptotic results for the energy density,

$$\frac{1}{8\pi}\langle b^2(\mathbf{r})\rangle_{m\leftarrow 0} \simeq \begin{cases} -\dfrac{7}{24\pi^2 k_0}\dfrac{|\mu^{m0}|^2}{r^7}, & k_0 r \gg 1 \\ \dfrac{5}{24\pi^2}k_0\dfrac{|\mu^{m0}|^2}{r^5}, & k_0 r \ll 1 . \end{cases} \tag{2.51}$$

III. INTERMOLECULAR ENERGY SHIFTS FROM ENERGY DENSITIES

In Sec. II we found the electric and magnetic energy densities associated with electric-dipole transitions in a source atom or molecule. The presence of these densities can be detected by their effect on polarizable test bodies placed in the neighborhood of the source. These densities can therefore be used in the determination of the interaction energy between two molecules.

A. Dispersion forces

We first consider the case where both molecules are in their ground states. The energy density arising from molecule A influences molecule B. The latter responds to the energy density at $\mathbf{R}_B$ for the transition $m\leftarrow 0$ (in A) through its dynamical polarizability at frequency ω_{m0}. Similarly, A responds to B for the transition $r\leftarrow 0$. Thus the total interaction energy from the pair with isotropic polarizabilities $\alpha^A(\omega)$ and $\alpha^B(\omega)$ is given by the expectation value of

$$\Delta E = -\tfrac{1}{2}\sum_m \alpha^B(\omega_{m0})\mathbf{d}^2_{m\leftarrow 0}(\mathbf{R}_B) - \tfrac{1}{2}\sum_r \alpha^A(\omega_{r0})\mathbf{d}^2_{r\leftarrow 0}(\mathbf{R}_A) , \tag{3.1}$$

where

$$\alpha^A(\omega) = \tfrac{2}{3}\sum_m \frac{E_{m0}|\mu^{m0}(A)|^2}{E_{m0}^2-(\hbar\omega)^2} . \tag{3.2}$$

Hence using (2.30) for the energy density and (3.2) for the polarizability we obtain, with $R=|\mathbf{R}_B-\mathbf{R}_A|$,

$$\Delta E=-\frac{4}{9\pi\hbar c}\int_0^\infty\sum_{m,r}\left[\frac{k_{r0}|\boldsymbol{\mu}^{r0}(B)|^2}{k_{r0}^2-k_{m0}^2}\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^2}{k_{m0}^2+u^2}+\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^2}{k_{m0}^2-k_{r0}^2}\frac{k_{r0}|\boldsymbol{\mu}^{r0}(B)|^2}{k_{r0}^2+u^2}\right]$$

$$\times u^6e^{-2uR}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right]du \tag{3.3}$$

$$=-\frac{4}{9\pi\hbar c}\sum_{m,r}\int_0^\infty\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^2k_{r0}|\boldsymbol{\mu}^{r0}(B)|^2}{(k_{m0}^2+u^2)(k_{r0}^2+u^2)}u^6e^{-2uR}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right]du\ , \tag{3.4}$$

which in terms of polarizabilities defined for imaginary frequencies is

$$\Delta E=-\frac{\hbar c}{\pi}\int_0^\infty\alpha^A(iu)\alpha_B(iu)u^6e^{-2uR}\times\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right]du\ . \tag{3.5}$$

This is the familiar Casimir-Polder interaction energy between two molecules in their ground states.

The interaction energy between a molecule A with an electric-dipole polarizability $\alpha^A(\omega)$ and another molecule B with a magnetic $\chi^B(\omega)$ can be found in a similar manner. The analog of (3.1) for the interaction energy is

$$\Delta E=-\tfrac{1}{2}\sum_m\chi^B(\omega_{m0})\mathbf{b}^2_{m\leftarrow 0}(\mathbf{R}_B)-\tfrac{1}{2}\sum_r\alpha^A(\omega_{r0})\mathbf{d}^2_{r\leftarrow 0}(\mathbf{R}_A)\ , \tag{3.6}$$

where $(1/8\pi)\mathbf{b}^2_{m\leftarrow 0}(\mathbf{r})$ is the magnetic energy density (2.50) due to the electric transition dipole $\mu^{m0}(A)$ and $(1/8\pi)\mathbf{d}^2_{r\leftarrow 0}(\mathbf{r})$ is, in this case, the electric energy density arising from a *magnetic* transition dipole $\mathbf{m}^{r0}(B)$. The interaction energy is found to be

$$\Delta E=\frac{4}{9\pi\hbar c}\int_0^\infty\sum_{m,r}\left[\frac{k_{r0}|\mathbf{m}^{r0}(B)|^2}{k_{r0}^2-k_{m0}^2}\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^2}{k_{m0}^2+u^2}+\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^2}{k_{m0}^2-k_{r0}^2}\frac{k_{r0}|\mathbf{m}^{r0}(B)|^2}{k_{r0}^2+u^2}\right]$$

$$\times u^6e^{-2uR}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{1}{u^4R^4}\right]du \tag{3.7}$$

$$=\frac{\hbar c}{\pi}\int_0^\infty\alpha^A(iu)\chi^B(iu)u^6e^{-2uR}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{1}{u^4R^4}\right]du\ , \tag{3.8}$$

in agreement with earlier work [9,10].

B. Intermolecular forces involving electronically excited molecules

It is straightforward to extend the calculations in III A to include electronically excited molecules. The response formalism involving the use of (3.1) and its analogs provides a direct route to obtain these interaction energies. These potentials are not easily obtainable by conventional methods because of intermediate-state resonances. In the response method these resonances do not pose any problems as they are automatically taken into account with the use of the *total* electromagnetic fields in the neighborhood of the sources. These fields include terms arising from real transitions. Further, it is easy to identify and interpret the terms that arise from such intermediate resonances.

1. Interaction between a ground-state molecule and an electronically excited molecule

In this subsection we consider molecule A to be in its ground state and B to be in the excited state $|p\rangle$; the transition $0\leftarrow p$ is assumed to be electric dipole allowed. Also the molecules are taken to be nonidentical. Then

$$\Delta E=-\tfrac{1}{2}\sum_m\alpha^B(\omega_{m0})\mathbf{d}^2_{m\leftarrow 0}(\mathbf{R}_B)-\tfrac{1}{2}\sum_r\alpha^A(\omega_{rp})\mathbf{d}^2_{r\leftarrow p}(\mathbf{R}_A)\ . \tag{3.9}$$

This expression differs from (3.1) in that $\mathbf{d}_{r\leftarrow p}(\mathbf{r})$ for downward transitions has terms associated with real photon emission and $\alpha^B(\omega)$ is now the dynamic polarizability for the excited molecule B. We have

$$\Delta E=-\tfrac{1}{2}\sum_{m}\alpha^{B}(\omega_{m0})\mathbf{d}^{2}_{m\leftarrow 0}(\mathbf{R}_{B})$$
$$-\tfrac{1}{2}\sum_{\substack{r\\E_r>E_p}}\alpha^{A}(\omega_{rp})\mathbf{d}^{2}_{r\leftarrow p}(\mathbf{R}_{A})$$
$$-\tfrac{1}{2}\sum_{\substack{r\\E_r<E_p}}\alpha^{A}(\omega_{rp})\mathbf{d}^{2}_{r\leftarrow p}(\mathbf{R}_{A})\ . \qquad (3.10)$$

We see from (2.36) and (2.39) that the third term in (3.10) gives (3.11) as the contribution from real photon emission:

$$-\frac{4}{9\hbar cR^{2}}\sum_{\substack{m,r\\E_r<E_p}}\frac{k_{m0}|\boldsymbol{\mu}^{r0}(B)|^{2}k_{pr}^{4}|\boldsymbol{\mu}^{m0}(A)|^{2}}{(k_{m0}^{2}-k_{pr}^{2})}\times\left[1+\frac{1}{k_{pr}^{2}R^{2}}+\frac{3}{k_{pr}^{4}R^{4}}\right], \qquad (3.11)$$

where we have expressed the polarizability of A in terms of transition dipole moments using (3.2). It is important to note that for large R the lead term of (3.11) has an R^{-2} dependence. This is the dominant interaction energy since the virtual photon terms show the well-known R^{-7} dependence in this limit. Thus for large R

$$\Delta E=\frac{4}{9\hbar cR^{2}}\sum_{\substack{m,r\\E_r<E_p}}\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^{2}k_{pr}^{4}|\boldsymbol{\mu}^{rp}(B)|^{2}}{(k_{m0}^{2}-k_{pr}^{2})}$$
$$=-\frac{2}{3R^{2}}\sum_{\substack{r\\E_r<E_p}}\alpha^{A}(\omega_{pr})|\boldsymbol{\mu}^{pr}(B)|^{2}k_{pr}^{4}\ . \qquad (3.12)$$

This result has a simple physical interpretation based on the Poynting vector. We note from (2.17) that the rate of energy loss out of a sphere centered at B due to the downward transition $r\leftarrow p$ is

$$\int\mathbf{S}\cdot\hat{\mathbf{R}}R^{2}d\Omega=\frac{4c}{3}|\boldsymbol{\mu}^{rp}|^{2}k_{pr}^{4}\ , \qquad (3.13)$$

where $\bar{\mathbf{S}}$ is the Poynting vector for a randomly oriented transition moment. Then, as to be expected,

$$\Delta E=-\frac{1}{2c}\alpha^{A}(\omega_{pr})\int\mathbf{S}\cdot\hat{\mathbf{R}}\,d\Omega=-2\pi\alpha W(R)\ , \qquad (3.14)$$

where the energy density $W(R)$ of the source-dependent field at $\mathbf{R}$ is $(1/4\pi c)\int\bar{\mathbf{S}}\cdot\hat{\mathbf{R}}\,d\Omega$. The virtual-photon contributions to the energy shift (3.10) remain to be discussed. Their structure is essentially the same as that of the upward transitions given in Sec. III A for the dispersion force. So ΔE has, in addition to (3.11), terms from all three sums in (3.10) giving

$$-\frac{4}{9\pi\hbar c}\sum_{m,r}\int_{0}^{\infty}\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^{2}k_{rp}|\boldsymbol{\mu}^{rp}(B)|^{2}}{(k_{m0}^{2}+u^{2})(k_{rp}^{2}+u^{2})}\times u^{6}e^{-2uR}\left[\frac{1}{u^{2}R^{2}}+\frac{2}{u^{3}R^{3}}+\frac{5}{u^{4}R^{4}}+\frac{6}{u^{5}R^{5}}+\frac{3}{u^{6}R^{6}}\right]du\ , \qquad (3.15)$$

where the summation over r includes both upward and *downward* transitions. This can be expressed as an integral analogous to (3.5), namely

$$\Delta E=-\frac{\hbar c}{\pi}\int_{0}^{\infty}\alpha^{A}(iu)\alpha^{B}(iu;p)u^{6}e^{-2uR}\times\left[\frac{1}{u^{2}R^{2}}+\frac{2}{u^{3}R^{3}}+\frac{5}{u^{4}R^{4}}+\frac{6}{u^{5}R^{5}}+\frac{3}{u^{6}R^{6}}\right]du\ , \qquad (3.16)$$

where $\alpha^{B}(\omega;p)$ is the dynamic polarizability for the excited state $|p\rangle$ of B and is given by

$$\alpha^{B}(\omega;p)=\frac{2}{3}\sum_{r}\frac{E_{rp}|\boldsymbol{\mu}^{rp}(B)|^{2}}{E_{rp}^{2}-(\hbar\omega)^{2}}\ . \qquad (3.17)$$

The third term in (3.10) giving the contributions from downward transitions is made up of two parts: one associated with real-photon transfer, given by (3.11), and the other associated with virtual photons from the downward transition part of (3.15). For large R, the leading term of (3.15) is

$$-\frac{23\hbar c}{4\pi}\frac{\alpha^{A}(0)\alpha^{B}(0;p)}{R^{7}}\ , \qquad (3.18)$$

where $\alpha^{A}(0)$ is the static polarizability of A given by (3.2) for $\omega=0$; similarly $\alpha^{B}(0;p)$ is the $\omega=0$ limit of (3.17). For small R, the dominant term of (3.15) is

$$-\frac{2}{3R^{6}}\sum_{m,r}\mathrm{sgn}(E_{rp})\frac{|\boldsymbol{\mu}^{m0}(A)|^{2}|\boldsymbol{\mu}^{rp}(B)|^{2}}{(E_{m0}+|E_{rp}|)}\ . \qquad (3.19)$$

The total interaction energy valid for all separations beyond electron overlap between A and B is the sum of the real-photon term (3.11) and the virtual-photon term (3.16) which can be expressed in terms of the f and g functions (2.25). For the sake of completeness we give the explicit result

$$\Delta E=-\frac{\hbar c}{\pi}\int_0^\infty \alpha^A(iu)\alpha^B(iu;p)u^6 e^{-2uR}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right]du$$

$$-\frac{4}{9\hbar c R^2}\sum_{\substack{m,r\\ E_r<E_p}}\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^2k_{pr}^4|\boldsymbol{\mu}^{rp}(B)|^2}{(k_{m0}^2-k_{pr}^2)}\left[1+\frac{1}{k_{pr}^2R^2}+\frac{3}{k_{pr}^4R^4}\right] \qquad (3.20)$$

$$=-\frac{1}{2\pi\hbar c R^2}\sum_{m,r}\left[\frac{2}{3}\right]^2\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^2k_{rp}|\boldsymbol{\mu}^{rp}(B)|^2}{(k_{m0}^2-k_{rp}^2)}$$

$$\times\left\{k_{m0}^3\left[\frac{1}{k_{m0}R}+f(2k_{m0}R)\left[-2+\frac{10}{k_{m0}^2R^2}-\frac{6}{k_{m0}^4R^4}\right]+g(2k_{m0}R)\left[\frac{4}{k_{m0}R}-\frac{12}{k_{m0}^3R^3}\right]\right]\right.$$

$$-|k_{rp}|^3\left[\frac{1}{|k_{rp}|R}+f(2|k_{rp}|R)\left[-2+\frac{1}{|k_{rp}|^2R^2}-\frac{6}{|k_{rp}|^4R^4}\right]\right.$$

$$\left.\left.+g(2|k_{rp}|R)\left[\frac{4}{|k_{rp}|R}-\frac{12}{|k_{rp}|^3R^3}\right]\right]\right\}$$

$$-\frac{1}{\hbar c R^2}\sum_{\substack{m,r\\ E_r<E_p}}\left[\frac{2}{3}\right]^2\frac{k_{m0}|\boldsymbol{\mu}^{m0}(A)|^2k_{pr}|\boldsymbol{\mu}^{rp}(B)|^2}{(k_{m0}^2-k_{pr}^2)}\left[k_{pr}^3\left[1+\frac{1}{k_{pr}^2R^2}+\frac{3}{k_{pr}^4R^4}\right]\right]. \qquad (3.21)$$

From the general result (3.21) we now find the asymptotic expressions for ΔE. In the small-R limit, using (3.19) for the asymptotic value of the first term we have

$$\Delta E\simeq-\frac{2}{3R^6}\sum_{m,r}\mathrm{sgn}(E_{rp})\frac{|\boldsymbol{\mu}^{m0}(A)|^2|\boldsymbol{\mu}^{rp}(B)|^2}{(E_{m0}+|E_{rp}|)}$$

$$-\frac{4}{3R^6}\sum_{\substack{m,r\\ E_r<E_p}}\frac{E_{m0}|\boldsymbol{\mu}^{rp}(B)|^2|\boldsymbol{\mu}^{m0}(A)|^2}{(E_{m0}^2-E_{pr}^2)}$$

$$=-\frac{2}{3R^6}\sum_{m,r}\frac{|\boldsymbol{\mu}^{m0}(A)|^2|\boldsymbol{\mu}^{rp}(B)|^2}{(E_{m0}+E_{rp})}\ . \qquad (3.22)$$

It is interesting to note that in this limit both real- and virtual-photon terms contribute to the R^{-6}-dependent energy (3.22). This is in contrast to the far-zone behavior where the dominant R^{-2} term arises solely from the real-photon exchange. With the aid of the asymptotic expansions (3.23) and (3.24) for $f(x)$ and $g(x)$ for large x [7]

$$f(x)\simeq\frac{1}{x}\left[1-\frac{2!}{x^2}+\frac{4!}{x^4}-\cdots\right], \qquad (3.23)$$

$$g(x)\simeq\frac{1}{x^2}\left[1-\frac{3!}{x^2}+\frac{5!}{x^4}-\cdots\right], \qquad (3.24)$$

the first summand in (3.21) can be seen to vary as R^{-7}. The second summand associated with real-photon exchange has a lead term proportional to R^{-2}, as found previously in (3.12).

2. *Interaction between two electronically excited molecules*

It is straightforward to extend the method to this case. The starting point for the calculation of the interaction energy between molecule A in state $|q\rangle$ and B in the $|p\rangle$ is the modified form of (3.9), namely

$$\Delta E=-\tfrac{1}{2}\sum_m \alpha^B(\omega_{mq})\mathbf{d}^2_{m\leftarrow q}(\mathbf{R}_B)$$

$$-\tfrac{1}{2}\sum_r \alpha^A(\omega_{rp})\mathbf{d}^2_{r\leftarrow p}(\mathbf{R}_A)\ , \qquad (3.25)$$

where both polarizabilities now refer to the excited molecules. In Sec. II we found expressions for the electric energy density associated with both upward and downward transitions. Using expression (2.39) for upward and (2.38) for downward transitions in (3.25) we obtain

$$
\begin{aligned}
\Delta E = &-\frac{1}{2\pi\hbar c R^2}\sum_{m,r}\left[\frac{2}{3}\right]^2 \frac{k_{mq}|\boldsymbol{\mu}^{mq}(A)|^2 k_{rp}|\boldsymbol{\mu}^{rp}(B)|^2}{(k_{mq}^2-k_{rp}^2)} \\
&\times\left\{|k_{mq}|^3\left[\frac{1}{|k_{mq}R|}+f(2|k_{mq}|R)\left[-2+\frac{10}{|k_{mq}|^2R^2}-\frac{6}{|k_{mq}|^4R^4}\right]\right.\right. \\
&\qquad\left.+g(|2k_{mq}|R)\left[\frac{4}{|k_{mq}|R}-\frac{12}{|k_{mq}|^3R^3}\right]\right] \\
&\quad-|k_{rp}|^3\left[\frac{1}{|k_{rp}|R}+f(2|k_{rp}|R)\left[-2+\frac{10}{|k_{rp}|^2R^2}-\frac{6}{|k_{rp}|^4R^4}\right]\right. \\
&\qquad\left.\left.+g(2|k_{rp}|R)\left[\frac{4}{|k_{rp}|R}-\frac{12}{|k_{rp}|^3R^3}\right]\right]\right\} \\
&-\frac{1}{\hbar c R^2}\sum_{\substack{m,r\\ E_r<E_p}}\left[\frac{2}{3}\right]^2 \frac{k_{mq}|\boldsymbol{\mu}^{mq}(A)|^2 k_{pr}|\boldsymbol{\mu}^{rp}(B)|^2}{(k_{mq}^2-k_{pr}^2)}\left[k_{pr}^3\left[1+\frac{1}{k_{pr}^2R^2}+\frac{3}{k_{pr}^4R^4}\right]\right] \\
&-\frac{1}{\hbar c R^2}\sum_{\substack{m,r\\ E_m<E_q}}\left[\frac{2}{3}\right]^2 \frac{k_{rp}|\boldsymbol{\mu}^{rp}(B)|^2 k_{qm}|\boldsymbol{\mu}^{mq}(A)|^2}{(k_{pr}^2-k_{mq}^2)}\left[k_{qm}^3\left[1+\frac{1}{k_{qm}^2R^2}+\frac{3}{k_{qm}^4R^4}\right]\right], \qquad (3.26)
\end{aligned}
$$

which can also be written in a form analogous to (3.20) as

$$
\begin{aligned}
\Delta E = &-\frac{\hbar c}{\pi}\int_0^\infty \alpha^A(iu;q)\alpha^B(iu;p)u^6 e^{-2uR}\left[\frac{1}{u^2R^2}+\frac{2}{u^3R^3}+\frac{5}{u^4R^4}+\frac{6}{u^5R^5}+\frac{3}{u^6R^6}\right]du \\
&-\frac{4}{9\hbar c R^2}\sum_{\substack{m,r\\ E_r<E_p}}\frac{k_{mq}|\boldsymbol{\mu}^{mq}(A)|^2 k_{pr}^4|\boldsymbol{\mu}^{rp}(B)|^2}{(k_{mq}^2-k_{pr}^2)}\left[1+\frac{1}{k_{pr}^2R^2}+\frac{3}{k_{pr}^4R^4}\right] \\
&-\frac{4}{9\hbar c R^2}\sum_{\substack{m,r\\ E_m<E_q}}\frac{k_{rp}|\boldsymbol{\mu}^{rp}(B)|^2 k_{qm}^4|\boldsymbol{\mu}^{mq}(A)|^2}{(k_{pr}^2-k_{mq}^2)}\left[1+\frac{1}{k_{qm}^2R^2}+\frac{3}{k_{qm}^4R^4}\right]. \qquad (3.27)
\end{aligned}
$$

This interaction energy can be decomposed into three types of terms depending on whether the transitions $m \leftarrow q$ and $r \leftarrow p$ are both upward, one upward and one downward, or both downward. The first two types are similar to those presented in Secs. III A and III B 1 where their asymptotic behavior has been discussed. We now examine the asymptotic forms for the third type due to downward transitions in both molecules with $E_{qm}, E_{pr} > 0$. For small R the result from elementary perturbation theory gives a repulsive force with potential

$$
\frac{2}{3R^6}\sum_{\substack{m,r\\ (E_m<E_q,E_r<E_p)}}\frac{|\boldsymbol{\mu}^{mq}(A)|^2|\boldsymbol{\mu}^{rp}(B)|^2}{(E_{qm}+E_{pr})}. \qquad (3.28)
$$

However, in the present calculation this potential arises from the three summands in (3.26). The first term, from virtual-photon exchange, is in fact the negative of (3.28). The second and third, which arise from real-photon exchange, together give

$$
\begin{aligned}
&\frac{4}{3\hbar c R^6}\sum_{\substack{m,r\\ (E_m<E_q,E_r<E_p)}}\frac{|\boldsymbol{\mu}_{mq}(A)|^2|\boldsymbol{\mu}^{rp}(B)|^2}{(k_{qm}^2-k_{pr}^2)} \\
&\qquad\times k_{qm}k_{pr}\left[\frac{1}{k_{pr}}-\frac{1}{k_{qm}}\right] \\
&\qquad\quad=\frac{4}{3R^6}\sum_{\substack{m,r\\ (E_m<E_q,E_r<E_p)}}\frac{|\boldsymbol{\mu}^{mq}(A)|^2|\boldsymbol{\mu}^{rp}(B)|^2}{(E_{qm}+E_{pr})}, \qquad (3.29)
\end{aligned}
$$

and the result (3.28) follows. For large R the dominant term is proportional to R^{-2} and arises solely from real-photon exchange. The energy in this limit arises solely from the second and third summands in (3.27) and is

$$
\begin{aligned}
&-\left[\frac{2}{3}\right]^2\frac{1}{(\hbar c)^4R^2}\sum_{\substack{m,r\\ (E_m<E_q,E_r<E_p)}}\frac{|\boldsymbol{\mu}^{mq}(A)|^2|\boldsymbol{\mu}^{rp}(B)|^2}{(E_{qm}+E_{pr})} \\
&\qquad\times E_{qm}E_{pr}(E_{qm}^2+E_{qm}E_{pr}+E_{pr}^2). \qquad (3.30)
\end{aligned}
$$

As in Sec. III B 1, the R^{-2} behavior can be interpreted in terms of the power per unit area emitted by each molecule.

IV. DISCUSSION AND SUMMARY

We have developed in this paper a method for determining the intermolecular potential between two molecules which is applicable to the dispersion case as well as to the case where one or both molecules are excited. The method involves the determination of the energy density of the electromagnetic field in the neighborhood of the molecules. This energy density is the $\mathbf{r}=\mathbf{r}'$ limit of $(1/8\pi)$ times the trace of the electric-field correlation $\langle d_i(\mathbf{r})d_j(\mathbf{r}')\rangle$. This correlation as well as the magnetic-magnetic and electric-magnetic ones have been derived in Sec. II. The correlation functions for the case of an excited molecule with excitation energy E_{p0} include terms in addition to those for the ground-state molecule. These additional terms, as for example in (2.35), differ from the ground-state type in being modulated by sinusoidal oscillations with argument $(r-r')E_{p0}/\hbar c$. In the limit $\mathbf{r}=\mathbf{r}'$ the cosine term survives and the additional terms are now polynomials in r^{-1}. The corresponding energy densities are precisely those of a classical electric-dipole source as shown for the electric energy density in Sec. II B.

The intermolecular potentials found by the response approach using the energy densities are given in Sec. III. The interaction energy is found by the response of each molecule to the electric energy density of the other. For a ground-state pair, this is given by (3.1) from which we recover the familiar retarded dispersion energy. This potential gives the London–van der Waals expression with an R^{-6} dependence for small R and the asymptotic Casimir expression with its R^{-7} dependence for large R. In the case with one or both molecules eletronically excited the response theory starts with (3.9) or (3.25) and leads to the intermolecular energy shift (3.20) or (3.27). These shifts are made up of two types of contributions: one similar to the dispersion expression associated with virtual-photon exchange and the other associated with real-photon exchange. In the former the polarizabilities now include downward transitions in addition to the upward ones; the R dependence of course is precisely that of the Casimir-Polder potential. The second contribution which arises from the energy density associated with real emission contains R^{-2}-, R^{-4}-, and R^{-6}-dependent terms. Thus for small R both types contribute to the R^{-6} potential, and together give the result expected from electrostatic theory. However, for large R we predict a new dependence on the separation, namely an R^{-2} energy shift coming from real photon exchange. As discussed in Sec. III B this has a physical interpretation based on the Poynting vector. This energy which falls away much slower than the London force can play an important role in physical phenomena involving excited chromophores separated by large distances within complex molecules.

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