

## Quantum electrodynamics with nonrelativistic sources. III. Intermolecular interactions

E. A. Power and T. Thirunamachandran

*Department of Mathematics and Department of Chemistry, University College London,  
London WC1H 0AJ, England*

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The multipolar formalism for a system of molecules developed in paper I (first preceding paper) is applied to a molecular pair to calculate the rate of energy transfer and intermolecular potential energies. In these calculations, one of the molecules is treated as passive when placed in the Maxwell field of the other. The electromagnetic field is calculated with the use of the Heisenberg picture as in paper II (second preceding paper). For resonance transfer between identical molecules, it is sufficient to consider the first-order fields to obtain the Förster rate. For nonidentical molecules, the probability of excitation transfer as a function of time is found with the use of the Heisenberg fields. A noteworthy feature of the calculations of dispersion energy is that with the use of electromagnetic fields, correct to quadratic terms in the transition moments, the complete Casimir-Polder intermolecular potential energy can be obtained by the consideration of one molecule as a test polarizable body in the field of the other.

## I. INTRODUCTION

In this paper we use the equations of motion for the electron and electromagnetic fields obtained in the preceding papers I and II (Ref. 1) to study the interactions between molecules. We consider the cases where both molecules are in their ground states or one is excited. In our development the Heisenberg picture is the natural choice, and the time evolution of the operators associated with the Maxwell fields and the electron fields are found from the equations of motion

$$i\hbar\dot{a} = \hbar\omega a + i \left[ \frac{2\pi\hbar ck}{V} \right]^{1/2} \vec{e}^{(\lambda)}(\vec{k}) \cdot \sum_{i,i'} [\vec{\mu}^{ii'}(A) b_i^A b_{i'}^{A\dagger} e^{-i\vec{k}\cdot\vec{R}_A} + \vec{\mu}^{ii'}(B) b_i^B b_{i'}^{B\dagger} e^{-i\vec{k}\cdot\vec{R}_B}], \quad (1.1)$$

$$i\hbar\dot{b}_n^A = E_n b_n^A - i \sum_{\vec{k},\lambda} \left[ \frac{2\pi\hbar ck}{V} \right]^{1/2} \vec{e}^{(\lambda)}(\vec{k}) \cdot \sum_m \vec{\mu}^{nm}(A) (a e^{i\vec{k}\cdot\vec{R}_A} - a^\dagger e^{-i\vec{k}\cdot\vec{R}_A}), \quad (1.2)$$

with a similar equation holding for  $b_n^B$ .

To calculate the interaction between a pair of identical molecules, one of which is excited, the classical method has its analog in the Heisenberg picture where the unexcited molecule interacts with the electromagnetic field of the excited molecule. The energy shift due to their interaction is calculated in Sec. II A. It is remarkable that an extension of this viewpoint to calculate the interaction between two polarizable bodies gives the complete Casimir-Polder potential energy.<sup>2</sup> This energy is found by computing  $-\frac{1}{2}\alpha\vec{d}^2$  where  $\alpha$  is the polarizability of one of the molecules, treated as a test body, and  $\vec{d}$  is the displacement vector field of the other molecule. As is shown in Sec. III, the relevant terms involve the  $\vec{d}^{(2)}$  field which depends quadratically on the transition moments of the source molecule.

In Sec. II B, we calculate the probability of excitation transfer between two nonidentical molecules, again using the Heisenberg fields. The result shows a complicated oscillatory behavior in time which for certain limiting cases following the delay interval  $R/c$ , tends to familiar results. These are, for times long compared with molecular frequencies and nearly equal energy separation in the two molecules, that given by the Fermi golden rule, and for very short intervals after  $R/c$  that the growth of probability is the square of this interval.

## II. EXCITATION TRANSFER BETWEEN TWO MOLECULES

In the study of energy transfer between molecules in a medium, the fundamental microscopic process is the exchange of excitation between a molecular pair. For two molecules with one excited and the other in its ground state, it is well known that the coupling is fully retarded. If the molecule at  $\vec{R}_A$  is initially excited and that at  $\vec{R}_B$  is in its ground state, the probability that molecule  $B$  is found to be excited must satisfy the causality condition

$$P(t) = 0, \quad 0 < t < |\vec{R}_B - \vec{R}_A|/c. \quad (2.1)$$

For times greater than  $R/c$ ,  $R = |\vec{R}_B - \vec{R}_A|$ , we consider the values of  $P(t)$  for various types of systems. In Sec. II A we consider a pair of identical molecules and calculate the rate  $dP/dt$  using the Fermi golden rule. In Sec. II B we consider the general case where the two molecules are nonidentical; it is found that  $P(t)$  shows oscillatory behavior.

## A. A pair of identical molecules

The leading contribution to the matrix element for the transfer of excitation from an excited molecule  $A$  to another molecule  $B$  of the same species but in the ground

state can be obtained by treating the molecule  $B$  as a test dipole in field of molecule  $A$ . The Heisenberg displacement vector field due to  $A$  has already been found in paper II (Ref. 1) to be

$$d_i(\vec{r}, t) = d_i^0(\vec{r}, t) + \sum_{m,n} \mu_j^{mn}(A) \beta_m^{A\dagger}(0) \beta_n^A(0) (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \times \frac{e^{ik_{nm}(|\vec{r}-\vec{R}_A|-ct)}}{|\vec{r}-\vec{R}_A|} + \dots \quad (2.2)$$

For a transition  $|0\rangle \leftarrow |p\rangle$  for molecule  $A$ , the matrix element of  $d_i^{(1)}$  is

$$\frac{dP}{dt} = \frac{2\pi}{\hbar} \mu_i^{0p}(A) \mu_j^{p0}(B) \bar{\mu}_k^{0p}(A) \bar{\mu}_l^{p0}(B) \left[ (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \frac{e^{ik_{p0R}}}{R} \right] \left[ (-\nabla^2 \delta_{kl} + \nabla_k \nabla_l) \frac{e^{-ik_{p0R}}}{R} \right] \rho \quad (2.6)$$

For randomly oriented molecules, we have

$$\frac{dP}{dt} = \frac{4\pi\rho}{9\hbar R^6} |\mu^{p0}(A)|^2 |\mu^{p0}(B)|^2 [3 + (kR)^2 + (kR)^4] \quad (2.7)$$

showing the Förster behavior<sup>3</sup> in the near zone. The  $R^{-2}$  dependence in the far zone is precisely the behavior to be expected from classical considerations. As already noted in Sec. II of paper II, the displacement vector field is equal to the total electric field outside the source. Thus the use of  $\vec{e}^{\text{tot}}(\vec{R}_B, t)$  which arises naturally in the minimal-coupling formalism, instead of  $\vec{d}(\vec{R}_B, t)$ , in (2.4) leads to the same rate (2.7).

### B. Direct calculation of excitation transfer between two nonidentical molecules

In contrast to the problem of energy exchange between identical molecules, it is not possible to express the excitation transfer in terms of a time-independent rate for a nonidentical pair. Hence the golden rule is not applicable,

$$\mu_j^{0p}(A) (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \frac{e^{ik_{p0}(|\vec{r}-\vec{R}_A|-ct)}}{|\vec{r}-\vec{R}_A|} \quad (2.3)$$

The interaction energy of the test dipole  $B$  having a transition moment  $\bar{\mu}^{p0}(B)$  with this field is

$$\Delta E = -\bar{\mu}^{p0}(B) e^{-i\omega_{op}t} \cdot \langle \vec{d}(\vec{R}_B, t) \rangle \quad (2.4)$$

$$= -\mu_j^{0p}(A) \mu_i^{p0}(B) (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \times \frac{e^{ik_{p0}|\vec{R}_B-\vec{R}_A|}}{|\vec{R}_B-\vec{R}_A|} \quad (2.5)$$

The rate of excitation transfer from  $A$  to  $B$  follows directly from the golden rule and equation (2.5),

and the primary quantity is the probability  $P(t)$ . For the initial conditions that molecule  $A$  is in an excited state and  $B$  in its ground state and the radiation field is the vacuum, the probability  $P(t)$  that  $A$  has decayed and molecule  $B$  is excited due to exchange of photons, but the final state of the radiation field is still a vacuum, is

$$P(t) = \langle i | b_g^{A\dagger}(t) b_q^{B\dagger}(t) \pi(t) b_q^B(t) b_g^A(t) | i \rangle \quad (2.8)$$

In (2.8)  $|i\rangle = |p; g; 0\rangle$  where the initial state of  $A$  is  $|p\rangle$  with energy  $E_{pg} (= \hbar c k_{pg} = \hbar \omega_A)$  and that of  $B$  is  $|g\rangle$ ; the vacuum state of the radiation field is represented by  $|0\rangle$ .  $\pi(t)$  is the projection operator at time  $t$  on to the vacuum of the composite system.

It is convenient to define the interaction representation operators

$$\alpha(t) = e^{-i\omega t} \alpha(t) \quad (2.9)$$

and

$$\beta_n(t) = e^{-iE_n t / \hbar} \beta_n(t) \quad (2.10)$$

From (1.1) and (1.2), we find the formal solutions,

$$\alpha(t) = \alpha(0) + \frac{1}{\hbar} \left[ \frac{2\pi \hbar c k}{V} \right]^{1/2} \left[ \sum_{m,n} \bar{\mu}^{mn}(A) \cdot \bar{\vec{e}} e^{-i\vec{k} \cdot \vec{R}_A} \int_0^t e^{i(\omega_{mn}^A + \omega)t'} \beta_m^{A\dagger}(t') \beta_n^A(t') dt' + \sum_{m,n} \bar{\mu}^{mn}(B) \cdot \bar{\vec{e}} e^{-i\vec{k} \cdot \vec{R}_B} \int_0^t e^{i(\omega_{mn}^B + \omega)t'} \beta_m^{B\dagger}(t') \beta_n^B(t') dt' \right] \quad (2.11)$$

$$\beta_n^A(t) = \beta_n^A(0) - \frac{1}{\hbar} \sum_{\vec{k}, \lambda} \left[ \frac{2\pi \hbar c k}{V} \right]^{1/2} \bar{\mu}^{nm}(A) \cdot \int_0^t [ \bar{\vec{e}} e^{i\vec{k} \cdot \vec{R}_A} e^{-i(\omega_{mn}^A + \omega)t'} \beta_m^A(t') \alpha(t') - \bar{\vec{e}} e^{-i\vec{k} \cdot \vec{R}_A} e^{-i(\omega_{mn}^A - \omega)t'} \beta_m^A(t') \alpha^\dagger(t') ] dt' \quad (2.12)$$

An equation similar to (2.12) holds for  $\beta_n^B(t)$ . Using these solutions, we calculate  $P(t)$  given by (2.8), correct to order  $[\mu(A)]^2$  and  $[\mu(B)]^2$ . Since  $\beta_g^B(0) |i\rangle = 0$ , we have, to order  $[\mu(A)]^2$ , and setting  $\vec{R}_A = 0$ ,

$$\begin{aligned}
P(t) &= \langle i | [\beta_g^{A\dagger}(t) - \beta_g^{A\dagger}(0)] \beta_q^{B\dagger}(t) \pi(t) \beta_q^B(t) [\beta_g^A(t) - \beta_g^A(0)] | i \rangle \\
&= \frac{1}{\hbar^2} \sum_{\substack{\vec{k}, \lambda, \\ \vec{k}', \lambda', \\ m, m'}} \left[ \frac{2\pi\hbar ck}{V} \right]^{1/2} \left[ \frac{2\pi\hbar ck'}{V} \right]^{1/2} \bar{\mu}_i^{gm}(A) \mu_j^{gm'}(A) \\
&\quad \times \left\langle i \left| \left[ \bar{e}_i \int_0^t e^{i(\omega_{mg}^A + \omega)t'} \beta_m^{A\dagger}(0) \alpha^\dagger(t') dt' - e_i \int_0^t e^{i(\omega_{mg}^A - \omega)t'} \beta_m^{A\dagger}(0) \alpha(t') dt' \right] \right. \right. \\
&\quad \times \beta_q^{B\dagger}(t) \pi(t) \beta_q^B(t) \left[ e_j \int_0^t e^{-i(\omega_{m'g}^A + \omega')t'} \beta_{m'}^A(0) \alpha'(t') dt' \right. \\
&\quad \left. \left. - \bar{e}_j \int_0^t e^{-i(\omega_{m'g}^A - \omega')t'} \beta_{m'}^A(0) \alpha'^\dagger(t') dt' \right] \right| i \rangle. \tag{2.13}
\end{aligned}$$

To proceed further, we first note that

$$\beta_q^B(t) \left[ e_j \int_0^t e^{-i(\omega_{m'g}^A + \omega')t'} \alpha'(t') dt' - \bar{e}_j \int_0^t e^{-i(\omega_{m'g}^A - \omega')t'} \alpha'^\dagger(t') dt' \right] \beta_{m'}^A(0) | i \rangle$$

has no terms independent of  $\mu(B)$ . It is therefore sufficient to substitute for  $\alpha'(t)$  and  $\beta(t)$  and collect terms of order  $\mu(B)$  and independent of  $\mu(A)$ . These are

$$\begin{aligned}
&\beta_q^B(0) \beta_m^{B\dagger}(0) \beta_g^B(0) \beta_p^A(0) | i \rangle \left[ e_j \int_0^t dt' e^{-i(\omega_A + \omega')t'} \frac{1}{\hbar} \left[ \frac{2\pi\hbar ck'}{V} \right]^{1/2} \mu_l^{mg}(B) \bar{e}_l e^{-i\vec{k}' \cdot \vec{R}} \int_0^{t'} dt'' e^{i(\omega_{mg}^B + \omega')t''} \right. \\
&\quad \left. - \bar{e}_j \int_0^{t'} dt' e^{-i(\omega_A - \omega')t'} \frac{1}{\hbar} \left[ \frac{2\pi\hbar ck'}{V} \right]^{1/2} \bar{\mu}_l^{gm}(B) e_l e^{i\vec{k}' \cdot \vec{R}} \int_0^{t'} dt'' e^{-i(\omega_{gm}^B + \omega')t''} \right] \\
&+ \sum_{\vec{k}'', \lambda''} \alpha''(0) \alpha'^\dagger(0) \beta_g^B(0) \beta_p^A(0) | i \rangle \\
&\quad \times \left[ \frac{1}{\hbar} \left[ \frac{2\pi\hbar ck''}{V} \right]^{1/2} \mu_l^{qg}(B) \int_0^t e_l e^{i\vec{k}'' \cdot \vec{R}} e^{i(\omega_B - \omega'')t'} dt' \bar{e}_j \int_0^t e^{-i(\omega_A - \omega')t'} dt' \right] \\
&+ \sum_{\vec{k}, \lambda} \alpha^\dagger(0) \alpha'^\dagger(0) \beta_g^B(0) \beta_p^A(0) | i \rangle \\
&\quad \times \left[ \frac{1}{\hbar} \left[ \frac{2\pi\hbar ck}{V} \right]^{1/2} \mu_l^{qg}(B) \int_0^t \bar{e}_l e^{-i\vec{k} \cdot \vec{R}} e^{i(\omega_B + \omega)t'} dt' \bar{e}_j \int_0^t e^{-i(\omega_A - \omega')t'} dt' \right]. \tag{2.14}
\end{aligned}$$

If (2.14) and its adjoint are inserted into (2.13),  $P(t)$  to order  $[\mu(A)]^2$  and  $[\mu(B)]^2$  may be obtained by approximating all operators by their values at  $t=0$ . For  $\pi(t)$ , this implies the projection onto the unperturbed vacuum for both the electron and radiation fields. Thus the last summand in (2.14) does not contribute to the process under consideration (it contributes to two-photon emission). Further, the second term of (2.14) contributes only when  $(\vec{k}'', \lambda'') = (\vec{k}', \lambda')$ . For the first term, it is clear that the contribution is nonzero only when  $m=q$ . Hence

$$\begin{aligned}
P(t) &= \left| \frac{1}{\hbar^2} \mu_j^{gp}(A) \sum_{\vec{k}, \lambda} \left[ \frac{2\pi\hbar ck}{V} \right] \left[ \mu_l^{qg}(B) e_j \bar{e}_l e^{-i\vec{k} \cdot \vec{R}} \int_0^t dt' e^{-i(\omega_A + \omega)t'} \int_0^{t'} dt'' e^{i(\omega_B + \omega)t''} \right. \right. \\
&\quad \left. \left. - \mu_l^{qg}(B) \bar{e}_j e_l e^{i\vec{k} \cdot \vec{R}} \left[ \int_0^t dt' e^{-i(\omega_A - \omega)t'} \int_0^{t'} dt'' e^{i(\omega_B - \omega)t''} \right. \right. \right. \\
&\quad \left. \left. \left. - \int_0^t dt' e^{i(\omega_B - \omega)t'} \int_0^{t'} dt'' e^{-i(\omega_A - \omega)t''} \right] \right] \right|^2 \tag{2.15}
\end{aligned}$$

which may be written as  $|c_{fi}(t)|^2$ , where

$$c_{fi}(t) = \frac{1}{\hbar^2} \mu_j^{gp}(A) \mu_i^{gq}(B) \sum_{\vec{k}, \lambda} \left[ \frac{2\pi\hbar c k}{V} \right] \left[ e_j \bar{e}_i e^{-i\vec{k} \cdot \vec{R}} \left( \frac{e^{i(\omega_B - \omega_A)t} - 1}{(\omega_B - \omega_A)(\omega_B + \omega)} + \frac{e^{-i(\omega_A + \omega)t} - 1}{(\omega_B + \omega)(\omega_B + \omega)} \right) \right. \\ \left. + \bar{e}_j e_i e^{i\vec{k} \cdot \vec{R}} \left( -\frac{e^{i(\omega_B - \omega_A)t}}{(\omega_B - \omega_A)(\omega_A - \omega)} + \frac{e^{i(\omega_B - \omega)t}}{(\omega_B - \omega)(\omega_A - \omega)} \right) \right]. \quad (2.16)$$

The sum over polarization directions and the angular integration over the  $\vec{k}$  direction are elementary. After dropping the rapidly oscillating terms, we get

$$c_{fi}(t) = \frac{1}{\hbar c} \mu_j^{gp}(A) \mu_i^{gq}(B) (-\nabla^2 \delta_{jl} + \nabla_j \nabla_l) \frac{1}{\pi R} \int_{-\infty}^{\infty} \sin(kR) \left[ \frac{e^{i(k_B - k_A)ct} - 1}{(k_B - k_A)(k - k_A)} + \frac{e^{i(k_B - k)ct} - 1}{(k - k_B)(k - k_A)} \right] dk \quad (2.17)$$

$$= \begin{cases} 0, & t < R/c \\ \frac{\mu_j^{gp}(A) \mu_i^{gq}(B)}{\hbar c} (-\nabla^2 \delta_{jl} + \nabla_j \nabla_l) \frac{1}{R} \frac{e^{ik_B ct}}{(k_B - k_A)} (e^{ik_A(R-ct)} - e^{ik_B(R-ct)}), & t > R/c. \end{cases} \quad (2.18)$$

Hence for  $t > R/c$ ,

$$P(t) = \left[ \frac{\mu_j^{gp}(A) \mu_i^{gq}(B)}{\hbar c (k_B - k_A)} (-\nabla^2 \delta_{jl} + \nabla_j \nabla_l) \frac{1}{R} \right. \\ \left. \times (e^{ik_A(R-ct)} - e^{ik_B(R-ct)}) \right]^2. \quad (2.19)$$

It is of interest to examine the limiting behavior of (2.19). For small  $\tau = t - R/c$ , and for randomly oriented molecules,

$$P(t) = \frac{2}{3} \frac{1}{\hbar^2} \frac{|\mu^{gp}(A)|^2 |\mu^{gq}(B)|^2}{R^6} \tau^2 = \frac{1}{\hbar^2} |\mathcal{V}|^2 \tau^2 \quad (2.20)$$

as expected. In (2.20),  $\mathcal{V}$  is the averaged near-zone potential between the dipoles. For large  $\tau$ ,  $P(t)$  is oscillatory and (2.19) leads to the Fermi-rule result (2.6) for  $k_B \simeq k_A$ , since

$$P(t) = \left[ \mu_j^{gp}(A) \mu_i^{gq}(B) (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \frac{1}{R} e^{ik_A R} \right]^2 \\ \times \left| \frac{e^{-iE_{fi}t/\hbar} - 1}{E_{fi}} \right|^2. \quad (2.21)$$

### III. INTERACTION BETWEEN TWO POLARIZABLE SYSTEMS

The interaction energy between two molecules in their ground states, i.e., the van der Waals energy, is proportional to  $R^{-6}$  in the near zone (London dispersion energy) and proportional to  $R^{-7}$  in the far zone (Casimir energy). Casimir and Polder<sup>2</sup> found the complete interaction energy valid for all separations outside the overlap region. In this section, we obtain their result in a simple manner using the Heisenberg fields of paper II. Molecule  $B$  is treated as a test polarizable body and its interaction with the field due to molecule  $A$  is evaluated using

$$\Delta E = -\frac{1}{2} \alpha^B \vec{d}^2(\vec{R}_B, t). \quad (3.1)$$

For simplicity we discuss the case where both molecules have isotropic polarizabilities. Using the expansion of the field of molecule  $A$  in powers of transition moments as in paper II, we have

$$\Delta E = -\frac{1}{2} \alpha^B [\vec{d}^{(0)}(\vec{R}_B, k) + \vec{d}^{(1)}(\vec{R}_B, t) + \vec{d}^{(2)}(\vec{R}_B, t) + \dots]^2 \\ = -\frac{1}{2} \alpha^B \vec{d}^{(0)} \cdot \vec{d}^{(0)} - \frac{1}{2} \alpha^B (\vec{d}^{(1)} \cdot \vec{d}^{(0)} + \vec{d}^{(0)} \cdot \vec{d}^{(1)}) - \frac{1}{2} \alpha^B \vec{d}^{(1)} \cdot \vec{d}^{(1)} - \frac{1}{2} \alpha^B (\vec{d}^{(2)} \cdot \vec{d}^{(0)} + \vec{d}^{(0)} \cdot \vec{d}^{(2)}) + \dots \quad (3.2)$$

The important contributions to the interaction energy arise from the fourth term of (3.2). It is clear that the first term of (3.2) does not contribute to the mutual interaction energy as  $\vec{d}^{(0)}$  is the free field and is independent of molecule  $A$ . The second term also does not contribute because it changes the photon number. The third term is clearly important for intermolecular calculations involving molecules in their excited states, since  $\vec{d}^{(1)}$  is then the classical field for real transitions from the excited states of the dipoles. However, for nonresonant cases, as when both molecules are their ground states, we can omit this term together with the resonant-type terms of  $\vec{d}^{(2)}$ .

For the calculation of the energy shift when the molecule is in its ground state  $|0\rangle$  and electromagnetic field is the vacuum state, we find the expectation value of the fourth term of (3.2) using the polarizability-dependent part of  $\vec{d}^{(2)}$  of Eq. (2.30) in paper II. We have

$$\begin{aligned}
& -\frac{1}{2} \langle 0;0 | \alpha^B(\vec{d}^{(2)} \cdot \vec{d}^{(0)} + \vec{d}^{(0)} \cdot \vec{d}^{(2)}) | 0;0 \rangle \\
& = -\frac{1}{2} \sum_{\vec{k}, \lambda} \langle 0;0 | \alpha^B d_i^{(2)}(\vec{R}_B, t) | 0; \vec{k}, \lambda \rangle \langle \vec{k}, \lambda; 0 | d_i^{(0)}(\vec{R}_B, t) | 0;0 \rangle + \text{c.c.} \\
& = -\frac{1}{2} \sum_{\vec{k}, \lambda} \left[ i \left[ \frac{2\pi\hbar c k}{V} \right]^{1/2} e_j e^{-i\omega t} \alpha^A(\omega) \alpha^B(\omega) (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \frac{e^{ikR}}{R} \right] \left[ (-i) \left[ \frac{2\pi\hbar c k}{V} \right]^{1/2} \bar{e}_i e^{-i\vec{k} \cdot \vec{R}} e^{i\omega t} \right] + \text{c.c.} \\
& = -\frac{1}{2} \sum_{\vec{k}} \alpha^A(\omega) \alpha^B(\omega) \left[ \frac{2\pi\hbar c k}{V} \right] (\delta_{ij} - \hat{k}_i \hat{k}_j) e^{-i\vec{k} \cdot \vec{R}} (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \frac{e^{ikR}}{R} + \text{c.c.} , \tag{3.3}
\end{aligned}$$

where  $\vec{R} = \vec{R}_B - \vec{R}_A$ .

In terms of the tensors  $\tau_{ij}(kR)$  and  $\sigma_{ij}(kR)$  defined by Eqs. (3.4) and (3.5),

$$\begin{aligned}
\tau_{ij}(kR) &= \frac{1}{4\pi} \int (\delta_{ij} - \hat{k}_i \hat{k}_j) e^{-i\vec{k} \cdot \vec{r}} dr \\
&= (\delta_{ij} - \hat{R}_i \hat{R}_j) \frac{\sin(kR)}{kR} + (\delta_{ij} - 3\hat{R}_i \hat{R}_j) \left[ \frac{\cos(kR)}{k^2 R^2} - \frac{\sin(kR)}{k^3 R^3} \right], \tag{3.4}
\end{aligned}$$

$$\begin{aligned}
\sigma_{ij}(kR) &= (-\nabla^2 \delta_{ij} + \nabla_i \nabla_j) \frac{\cos(kR)}{k^3 R} \\
&= (\delta_{ij} - \hat{R}_i \hat{R}_j) \frac{\cos(kR)}{kR} - (\delta_{ij} - 3\hat{R}_i \hat{R}_j) \left[ \frac{\sin(kR)}{k^2 R^2} + \frac{\cos(kR)}{k^3 R^3} \right], \tag{3.5}
\end{aligned}$$

this interaction energy becomes

$$\Delta E = -\frac{\hbar c}{\pi} \int_0^\infty \alpha^A(\omega) \alpha^B(\omega) \tau_{ij}(kR) \sigma_{ij}(kR) k^6 dk \tag{3.6}$$

$$= -\frac{\hbar c}{\pi R^2} \text{Im} \int_0^\infty \alpha^A(\omega) \alpha^B(\omega) \left[ 1 + \frac{2i}{kR} - \frac{5}{k^2 R^2} - \frac{6i}{k^3 R^3} + \frac{3}{k^4 R^4} \right] e^{2ikR} k^4 dk . \tag{3.7}$$

In terms of polarizabilities expressed as functions of imaginary frequency  $\omega = ck = icu$ , (3.7) is

$$-\frac{\hbar c}{\pi R^2} \int_0^\infty u^4 \alpha^A(icu) \alpha^B(icu) e^{-2uR} \left[ 1 + \frac{2}{uR} + \frac{5}{u^2 R^2} + \frac{6}{u^3 R^3} + \frac{3}{u^4 R^4} \right] du . \tag{3.8}$$

In terms of the transition moments of molecules *A* and *B*, (3.8) may be written as

$$\begin{aligned}
& -\frac{\hbar c}{\pi R^2} \sum_n \frac{2k^{n0}}{3\hbar c} \mu^{0n}(A) \mu^{n0}(A) \sum_{n'} \frac{2k^{n'0}}{3\hbar c} \mu^{0n'}(B) \mu^{n'0}(B) \\
& \quad \times \int_0^\infty \frac{u^4 e^{-2uR}}{(k_{n0}^2 + u^2)(k_{n'0}^2 + u^2)} \left[ 1 + \frac{2}{uR} + \frac{5}{u^2 R^2} + \frac{6}{u^3 R^3} + \frac{3}{u^4 R^4} \right] du . \tag{3.9}
\end{aligned}$$

This is the complete expression of the Casimir-Polder potential<sup>2</sup> valid for all *R* outside the region of molecular overlap. In the far zone, this reduces to

$$-\frac{23\hbar c}{4\pi} \frac{\alpha^A \alpha^B}{R^7}, \tag{3.10}$$

where  $\alpha^A$  and  $\alpha^B$  are now static polarizabilities, whereas in the near zone, (3.9) gives the London energy (3.11),

$$-\frac{2}{3} \sum_{n, n'} \frac{\mu^{0n}(A) \mu^{n0}(A) \mu^{0n'}(B) \mu^{n'0}(B)}{\hbar c (k_{n0} + k_{n'0}) R^6}. \tag{3.11}$$

Although the asymptotic results may be obtained by other elementary methods,<sup>4-6</sup> the present approach of calculating the energy of a "test" molecule placed in the electromagnetic field of the other molecule gives the complete result applicable for all intermolecular separation.

<sup>1</sup>E. A. Power and T. Thirunamachandran, this issue, Phys. Rev. A **28**, 2649 (1983); preceding paper, *ibid.* **28**, 2663 (1983).

<sup>2</sup>H. B. G. Casimir and D. Polder, Phys. Rev. **46**, 407 (1949).

<sup>3</sup>T. Förster, Naturwissenschaften **33**, 166 (1946).

<sup>4</sup>H. B. G. Casimir, J. Chim. Phys. **46**, 407 (1949).

<sup>5</sup>D. P. Craig and E. A. Power, Int. J. Quantum Chem. **3**, 903 (1969).

<sup>6</sup>E. A. Power and D. F. Walls, Chem. Phys. Letts. **67**, 467 (1979).