PHYSICAL REVIEW A VOLUME 25, NUMBER 5 MAY 1982

Quantum electrodynamics in a cavity

E. A. Power and T. Thirunamachandran
Departments of Mathematics and Chemistry, University College London, London WC 1, England
(Received 28 July 1981)

The theory of interaction of atoms and molecules with radiation confined in a cavity is presented. The effect of the confinement on the field commutation relations is examined and the modified commutation relations are derived for an arbitrary cavity. It is shown that a canonical transformation on the minimal-coupling Hamiltonian for such systems leads to a new Hamiltonian containing explicitly neither the interatomic nor the atom image potentials. The new multipolar Hamiltonian is used to calculate energy shifts of an atom and a pair of atoms near a conducting wall. Changes in the rate of spontaneous emission from an excited atom are also evaluated.

I. INTRODUCTION

In recent years there has been considerable interest concerning the behavior of atoms and molecules near conducting surfaces. Theoretical analyses of the electrodynamics have been based on the minimal-coupling Hamiltonian. In this formalism, the electronic motions are coupled to the electromagnetic field through the vector potential. In addition to this coupling, the interaction Hamiltonian contains Coulomb terms representing electrostatic interactions between charges and with their images. It is well known that with the use of the multipolar form of the Hamiltonian in conventional electrodynamics, all interactions are mediated by transverse photons. The transformation from the minimal to the multipolar form eliminates the interatomic Coulomb interactions leaving only the intra-atomic electrostatic binding energies.[1,2] In general, calculations of processes involving atoms and radiation are simpler with the multipolar Hamiltonian than with the minimal coupling. In this paper we examine the effect of the cavity images on the transformation between the Hamiltonians, and show that this simplicity still holds. In a recent paper,[3] Barton has remarked that for an atom near a wall the two Hamiltonians lead to identical forces, although no formal demonstration of the equivalence was given. In the present work the equivalence becomes evident when viewed in terms canonical transformations.

The basic theory is outlined in the next section and the generalized field commutation relations are derived for an arbitrary cavity. As pointed out by Milloni,[4] the commutation relations for the case of a single conducting wall are different from those for free space. In addition to the transverse δ function depending on the separation between the field points, there are now additional terms depending on the separations between the field points and their images. The role of the images in the minimal-coupling formalism is discussed in Sec. III. In Sec. IV the canonical transformation of the minimal-coupling Hamiltonian to the multipolar form is described. It is shown that the image terms are completely removed by the transformation. The presence of the images is entirely felt by the mode functions for the radiation field in the cavity. In the final section, the multipolar formalism is applied to energy shifts of polarizable bodies and spontaneous emission rate for an excited atom near a conducting wall.

II. COMMUTATION RELATIONS FOR ELECTROMAGNETIC FIELDS CONFINED IN A CAVITY

The quantum theory of a free electromagnetic field in a cavity with conducting walls is most conveniently approached by expanding the electromagnetic field in terms of standing waves. The expansion coefficients oscillate sinusoidally and quantization is effected by promoting these coefficients to quantum operators subject to the standard commutation relations. Let $\vec{f}^{(\lambda)}(\vec{r})$ form a complete set of orthogonal transverse modes for the cavity. These satisfy the equations

$$\vec{\nabla}\cdot\vec{f}^{(\lambda)}(\vec{r})=0\,, \tag{1}$$

$$\vec{\nabla}\times\vec{\nabla}\times\vec{f}^{(\lambda)}(\vec{r})+(k^{(\lambda)})^2\vec{f}^{(\lambda)}(r)=0\,, \tag{2}$$

and are subject to the condition

$$\hat{\vec{n}}\times\vec{f}^{(\lambda)}(\vec{r})=0 \tag{3}$$

at the boundary. The label λ characterizes the mode. The electric and magnetic field expansions are

$$\vec{e}^{\perp}(\vec{r})=\left[\frac{4\pi}{V}\right]^{1/2}\sum_{\lambda}p_{\lambda}\vec{f}^{(\lambda)}(\vec{r}) , \tag{4}$$

$$\vec{b}(\vec{r})=\vec{\nabla}\times\vec{a}(\vec{r})$$
$$=-c\left[\frac{4\pi}{V}\right]^{1/2}\sum_{\lambda}q_{\lambda}\vec{\nabla}\times\vec{f}^{(\lambda)}(\vec{r}) , \tag{5}$$

where the normalization factor has been chosen such that

$$\frac{1}{V}\int\vec{f}^{(\lambda)}(\vec{r})\cdot\vec{f}^{(\lambda')}(\vec{r})d\vec{r}=\delta_{\lambda\lambda'} . \tag{6}$$

Since the p's and q's are canonically conjugate variables, the commutation relations for the fields are

$$[e_i^{\perp}(\vec{r}),a_j(\vec{r}')]=4\pi i\hbar c\frac{1}{V}\sum_{\lambda}f_i^{(\lambda)}(\vec{r})f_j^{(\lambda)}(\vec{r}') . \tag{7}$$

Noting that for $\vec{r}$ and $\vec{r}'$ within V

$$\frac{1}{V}\sum_{\lambda}[f_i^{(\lambda)}(\vec{r})f_j^{(\lambda)}(\vec{r}')+g_i^{(\lambda)}(\vec{r})g_j^{(\lambda)}(\vec{r}')]=\delta_{ij}\delta(\vec{r}-\vec{r}') \tag{8}$$

and

$$\delta_{ij}\delta(\vec{r}-\vec{r}')=\delta_{ij}^{\perp}(\vec{r}-\vec{r}')+\delta_{ij}^{\parallel}(\vec{r}-\vec{r}') , \tag{9}$$

where the $\vec{g}$'s form a complete orthonormal set of longitudinal mode functions, we write (7) as

$$[e_i^{\perp}(\vec{r}) ,a_j(\vec{r}')]=4\pi i\hbar c\left[\delta_{ij}^{\perp}(\vec{r}-\vec{r}')-\frac{1}{4\pi}\nabla_i\nabla_j\frac{1}{|\vec{r}-\vec{r}'|}-\frac{1}{V}\sum_{\lambda}g_i^{(\lambda)}(\vec{r})g_j^{(\lambda)}(\vec{r}')\right] . \tag{10}$$

Since the $\vec{g}^{(\lambda)}$'s are longitudinal mode functions, they can be written as

$$g_i^{(\lambda)}(\vec{r})=\frac{\nabla_i\phi^{(\lambda)}(\vec{r})}{k^{(\lambda)}} , \tag{11}$$

where the $\phi^{(\lambda)}$'s form a complete set of scalar functions satisfying

$$\nabla^2\phi^{(\lambda)}(\vec{r})+(k^{(\lambda)})^2\phi^{(\lambda)}(\vec{r})=0 . \tag{12}$$

Hence the commutator (10) is

$$4\pi i\hbar c\delta_{ij}^{\perp}(\vec{r}-\vec{r}')+i\hbar c\nabla_i\nabla_j'\left[\frac{1}{|\vec{r}-\vec{r}'|}-\frac{4\pi}{V}\sum_{\lambda}\frac{\phi^{(\lambda)}(\vec{r})\phi^{(\lambda)}(\vec{r}')}{(k^{(\lambda)})^2}\right] . \tag{13}$$

The second term in (13) which represents the boundary contribution can be expressed in terms of a distribution $\tilde{\theta}$ *exterior* to the cavity. For this purpose we define the function

$$\chi(\vec{r};\vec{r}')=\frac{1}{|\vec{r}-\vec{r}'|}+\int_{\bar{V}}\frac{\tilde{\theta}(\vec{s};\vec{r}')}{|\vec{r}-\vec{s}|}d\vec{s} , \tag{14}$$

where $\tilde{\theta}(\vec{s};\vec{r}')$ is chosen such that, as a function of $\vec{s}$, it is zero inside the cavity, and also that $\chi(\vec{r};\vec{r}')$, as a function of $\vec{r}$, vanishes at the boundary. The symbol $\bar{V}$ emphasizes the fact that the integration over $\vec{s}$ is outside the cavity. Hence

$$i\hbar c\nabla_i\nabla_j'\left[\frac{1}{|\vec{r}-\vec{r}'|}-\frac{4\pi}{V}\sum_{\lambda}\frac{\phi^{(\lambda)}(\vec{r})\phi^{(\lambda)}(\vec{r}')}{(k^{(\lambda)})^2}\right]=-i\hbar c\nabla_i\nabla_j'\left[\int\frac{\tilde{\theta}(\vec{s};\vec{r}')}{|\vec{r}-\vec{s}|}d\vec{s}-\chi(\vec{r};\vec{r}')+\frac{4\pi}{V}\sum_{\lambda}\frac{\phi^{(\lambda)}(\vec{r})\phi^{(\lambda)}(\vec{r}')}{(k^{(\lambda)})^2}\right] . \tag{15}$$

For $\vec{r}$ and $\vec{r}'$ in V, it is evident that χ satisfies

$$\nabla^2\chi(\vec{r};\vec{r}')=-4\pi\delta(\vec{r}-\vec{r}')\,, \tag{16}$$

and that the ϕ's obey

$$\frac{1}{V}\sum_{\lambda}\phi^{(\lambda)}(\vec{r})\phi^{(\lambda)}(\vec{r}')=\delta(\vec{r}-\vec{r}')\,. \tag{17}$$

Hence

$$\nabla^2\left[\chi(\vec{r};\vec{r}')-\frac{4\pi}{V}\sum_{\lambda}\frac{\phi^{(\lambda)}(\vec{r})\phi^{(\lambda)}(\vec{r}')}{(k^{(\lambda)})^2}\right]=0\,, \tag{18}$$

which implies, since both terms are zero at the boundary, that

$$\chi(\vec{r};\vec{r}')-\frac{4\pi}{V}\sum_{\lambda}\frac{\phi^{(\lambda)}(\vec{r})\phi^{(\lambda)}(\vec{r}')}{(k^{(\lambda)})^2}=0\,. \tag{19}$$

Thus the commutation relations for the electromagnetic fields confined in a cavity are

$$[e_i^{\perp}(\vec{r})\,,a_j(\vec{r}')]=4\pi i\hbar c\delta_{ij}^{\perp}(\vec{r}-\vec{r}')-i\hbar c\nabla_i\nabla_j'\int\frac{\tilde{\theta}(\vec{s};\vec{r}')}{|\vec{r}-\vec{s}\,|}d\vec{s}\,. \tag{20}$$

We illustrate this general result by considering the special case of a rectangular parallelepiped where the field points are near one wall. For this case it is clear that

$$\chi(\vec{r};\vec{r}')=\frac{1}{|\vec{r}-\vec{r}'|}-\frac{1}{|\vec{r}-\sigma\vec{r}'|}\,. \tag{21}$$

Therefore

$$\tilde{\theta}(\vec{s};\vec{r}')=-\delta(\vec{s}-\sigma\vec{r}')\,, \tag{22}$$

where $\sigma\vec{r}'$ is the point corresponding to the reflection of the point $\vec{r}'$ in the wall. If we denote the image point of $\vec{r}'$ by $\tilde{r}'$, we have the explicit relationship

$$\tilde{r}_i'=\sigma_{ij}r_j'\,, \tag{23}$$

where, for example, if the wall is $z=0$,

$$\sigma=\begin{bmatrix}1&&\\&1&\\&&-1\end{bmatrix}. \tag{24}$$

Using (22) we get

$$\begin{aligned}\nabla_i\nabla_j'\int\frac{\tilde{\theta}(\vec{s};\vec{r}')}{|\vec{r}-\vec{s}\,|}d\vec{s}&=-\nabla_i\nabla_j'\frac{1}{|\vec{r}-\sigma\vec{r}'|}\\&=\sigma_{jk}\nabla_i\nabla_k\frac{1}{|\vec{r}-\sigma\vec{r}'|}\\&=-4\pi\sigma_{jk}\delta_{ki}^{\parallel}(\vec{r}-\sigma\vec{r}')\,.\end{aligned} \tag{25}$$

Since $\vec{r}$ and $\sigma\vec{r}'$ are never coincident, the longitudinal δ function is equal to the negative of the transverse δ function; thus

$$[e_i^{\perp}(\vec{r})\,,a_j(\vec{r}')]=4\pi i\hbar c[\delta_{ij}^{\perp}(\vec{r}-\vec{r}')-\sigma_{jk}\delta_{ki}^{\perp}(\vec{r}-\sigma\vec{r}')]\,. \tag{26}$$

When the wall is $z=0$, we have

$$\begin{aligned}&[e_x^{\perp}(\vec{r})\,,a_x(\vec{r}')]=4\pi i\hbar c[\delta_{xx}^{\perp}(\vec{r}-\vec{r}')-\delta_{xx}^{\perp}(\vec{r}-\tilde{\vec{r}}')]\,,\\&[e_y^{\perp}(\vec{r})\,,a_y(\vec{r}')]=4\pi i\hbar c[\delta_{yy}^{\perp}(\vec{r}-\vec{r}')-\delta_{yy}^{\perp}(\vec{r}-\tilde{\vec{r}}')]\,,\\&[e_z^{\perp}(\vec{r})\,,a_z(\vec{r}')]=4\pi i\hbar c[\delta_{zz}^{\perp}(\vec{r}-\vec{r}')+\delta_{zz}^{\perp}(\vec{r}-\tilde{\vec{r}}')]\,,\ \text{etc.},\end{aligned} \tag{27}$$

which are essentially the results of Milloni.[4] It may be mentioned that an alternative route to (26) is through the use of the explicit forms of the mode functions for a rectangular box.

III. HAMILTONIAN IN MINIMAL COUPLING FORM

Quantum electrodynamics deals with the interaction of radiation with charges, and the Hamiltonian for the combined dynamical system can be written as

$$H = H_{\text{kin}} + H_{\text{rad}} + H_{\text{int}} + V_{\text{Coulomb}} , \tag{28}$$

where H_{kin} is the kinetic energy of the charges, H_{rad} is the second-quantized Hamiltonian for the radiation field, and H_{int}, which represents the coupling of the electrons with the radiation field, is

$$H_{\text{int}} = \sum_{\text{electrons}} \left[\frac{e}{mc} \vec{p}\cdot\vec{a}(\vec{q}) + \frac{e^2}{2mc^2} \vec{a}^2(\vec{q}) \right] . \tag{29}$$

V_{Coulomb} is the contribution from the longitudinal component of the electric field and is given by

$$V_{\text{Coulomb}} = \frac{1}{8\pi} \int_V \vec{E}^{\parallel 2} d\vec{r} = -\frac{1}{8\pi} \int_V \phi \nabla^2 \phi \, d\vec{r} , \tag{30}$$

where

$$\phi(\vec{r}) = \int_V \frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|} d\vec{r}\,' + \int_{\bar{V}} \frac{\tilde{\rho}(\vec{s})}{|\vec{r}-\vec{s}|} d\vec{s} . \tag{31}$$

In Eq. (31) $\rho(\vec{r}\,')$ is the charge density and $\tilde{\rho}(\vec{s})$ is the fictitious charge distribution *external* to the cavity (image charges) ensuring that $\phi(\vec{r})$ vanishes at the conducting boundary. In fact, from (14) it follows that

$$\tilde{\rho}(\vec{s}) = \int \rho(\vec{r}\,')\tilde{\theta}(\vec{s};\vec{r}\,') d\vec{r}\,' . \tag{32}$$

Thus,

$$V_{\text{Coulomb}} = -\frac{1}{8\pi} \int_V \phi(\vec{r}) \left[-4\pi \int_V \rho(\vec{r}\,')\delta(\vec{r}-\vec{r}\,') d\vec{r}\,' - 4\pi \int_{\bar{V}} \tilde{\rho}(\vec{s})\delta(\vec{r}-\vec{s}) d\vec{s} \right] d\vec{r}$$
$$= \tfrac{1}{2} \int_V \int_V \frac{\rho(\vec{r})\rho(\vec{r}\,'')}{|\vec{r}-\vec{r}\,''|} d\vec{r}\,'' d\vec{r} + \tfrac{1}{2} \int_V \int_{\bar{V}} \frac{\tilde{\rho}(\vec{s})\rho(\vec{r})}{|\vec{r}-\vec{s}|} d\vec{s} d\vec{r} . \tag{33}$$

The first term in (33), ignoring self-energies, represents the electrostatic interactions between the real charge and may be partitioned into intra- and interatomic interaction terms in the usual manner. The second term represents the interaction between the real charges and the induced surface distribution, we call this V_{image}. Thus the Hamiltonian is

$$H = H_{\text{atoms}} + H_{\text{rad}} + H_{\text{int}} + V_{\text{inter}} + V_{\text{image}} . \tag{34}$$

We illustrate this result for the case of an atom near a wall. Denoting the position vector of the atom by $\vec{R}$, the charge distribution of the atom and the image distribution are given by

$$\rho(\vec{r}) = -e \sum_\alpha \delta(\vec{r}-\vec{q}_\alpha) + Ze\delta(\vec{r}-\vec{R}) , \tag{35}$$

$$\tilde{\rho}(\vec{s}) = e \sum_\alpha \delta(\vec{s}-\tilde{\vec{q}}_\alpha) - Ze\delta(\vec{s}-\tilde{\vec{R}}) , \tag{36}$$

where $\vec{q}_\alpha$ is the position vector of electron α and $\tilde{\vec{q}}_\alpha$ is the position vector of the image. Substituting for ρ and $\tilde{\rho}$ in (33) we get, ignoring self-energies,

$$V_{\text{Coulomb}} = -Ze^2 \sum_\alpha \frac{1}{|\vec{q}_\alpha - \vec{R}|} + e^2 \sum_{\alpha<\beta} \frac{1}{|\vec{q}_\alpha - \vec{q}_\beta|} + V_{\text{image}} , \tag{37}$$

where

$$V_{\text{image}} = -\frac{1}{2} \frac{Z^2e^2}{|\vec{R}-\tilde{\vec{R}}|} + \tfrac{1}{2} Ze^2 \sum_\alpha \frac{1}{|\vec{R}-\tilde{\vec{q}}_\alpha|} = \tfrac{1}{2} Ze^2 \sum_\alpha \frac{1}{|\vec{q}_\alpha - \tilde{\vec{R}}|} - \frac{e^2}{2} \sum_{\alpha<\beta} \frac{1}{|\vec{q}_\alpha - \tilde{\vec{q}}_\beta|} . \tag{38}$$

If $|\vec{R}| >> |\vec{q}_\alpha - \vec{R}|$, the expression for image can be expanded in a multipolar series, the leading term being

$$\frac{1}{2}\frac{\mu_i\tilde{\mu}_j}{|\vec{R}-\tilde{\vec{R}}|^5}[\delta_{ij}|\vec{R}-\tilde{\vec{R}}|^2-3(\vec{R}-\tilde{\vec{R}})_i(\vec{R}-\tilde{\vec{R}})_j], \tag{39}$$

where the dipole and its image are given by

$$\vec{\mu}=-e\sum_\alpha(\vec{q}_\alpha-\vec{R}), \tag{40}$$

$$\tilde{\vec{\mu}}=e\sum_\alpha(\tilde{\vec{q}}_\alpha-\tilde{\vec{R}})=-\sigma\vec{\mu}. \tag{41}$$

It is important to note the presence of the factor of $\frac{1}{2}$ in (39) in contrast to the expression for the potential energy between two real dipoles. In the early work of Lennard-Jones[5] on the attraction of an atom to a metal surface, this factor was not included which led to twice the correct value for the interaction energy, as was later pointed out by Bardeen.[6]

For a pair of dipoles at $\vec{R}_A$ and $\vec{R}_B$, the above results may be generalized to

$$V_{\text{inter}}=\frac{\mu_i^A\mu_j^B}{|\vec{R}_B-\vec{R}_A|}\beta_{ij}^{(\vec{R}_B-\vec{R}_A)}, \tag{42}$$

$$\begin{aligned}V_{\text{image}}=&\frac{1}{2}\frac{\mu_i^A\tilde{\mu}_j^A}{|\vec{R}_A-\vec{R}_A|^3}\beta_{ij}^{(\vec{R}_A-\tilde{\vec{R}}_A)}+\frac{1}{2}\frac{\mu_i^B\tilde{\mu}_j^B}{|\vec{R}_B-\vec{R}_B|^3}\beta_{ij}^{(\vec{R}_B-\tilde{\vec{R}}_B)}\\&+\frac{1}{2}\frac{\mu_i^A\tilde{\mu}_j^B}{|\vec{R}_A-\vec{R}_B|^3}\beta_{ij}^{(\vec{R}_A-\tilde{\vec{R}}_B)}+\frac{1}{2}\frac{\mu_i^B\tilde{\mu}_j^A}{|\vec{R}_B-\vec{R}_A|^3}\beta_{ij}^{(\vec{R}_B-\tilde{\vec{R}}_A)},\end{aligned} \tag{43}$$

where

$$\beta_{ij}^{(\vec{R})}=(\delta_{ij}-3\hat{R}_i\hat{R}_j). \tag{44}$$

IV. CANONICAL TRANSFORMATION TO MULTIPOLAR HAMILTONIAN

The transformation of the minimal coupling Hamiltonian to the multipolar form is effected through the generator

$$S=\frac{1}{\hbar c}\int\vec{p}(\vec{r})\cdot\vec{a}(\vec{r})d\vec{r}, \tag{45}$$

where $\vec{p}(\vec{r})$ is the polarization field for the atoms. We apply the same transformation to the Hamiltonian (34), with the fields obeying the new commutation relations (20):

$$H_{\text{mult}}=e^{-iS}He^{iS}. \tag{46}$$

The new field commutation relations do not affect the transformation of $H_{\text{kin}}+H_{\text{int}}$; hence, as in earlier work,[2,7] we have

$$e^{-iS}(H_{\text{kin}}+H_{\text{int}})e^{iS}=H_{\text{kin}}+H_{\text{mag}}+H_{\text{dia}}, \tag{47}$$

where

$$H_{\text{mag}}=-\int\vec{m}(\vec{r})\cdot\vec{b}(\vec{r})d\vec{r}, \tag{48}$$

$$H_{\text{dia}}=\tfrac{1}{2}\int\underline{Q}(\vec{r},\vec{r}'):\vec{b}(\vec{r})\vec{b}(\vec{r}')d\vec{r}d\vec{r}'. \tag{49}$$

$\vec{m}(\vec{r})$ and $\underline{Q}(\vec{r},\vec{r}')$ are the magnetization and dimagnetization fields, respectively.

The transformation of H_{rad} gives a series which terminates after three terms:

$$\begin{aligned}e^{-iS}H_{\text{rad}}e^{iS}=&H_{\text{rad}}-\frac{i}{\hbar c}\int p_i(\vec{r})[a_i(\vec{r}),H_{\text{rad}}]d\vec{r}\\&-\frac{1}{2(\hbar c)^2}\int\int p_i(\vec{r})p_j(\vec{r}')[a_i(\vec{r}),[a_j(\vec{r}'),H_{\text{rad}}]]d\vec{r}d\vec{r}'.\end{aligned} \tag{50}$$

To evaluate the commutators, H_{rad} should be expressed in terms of the canonically conjugate fields $\vec{\Pi}(\vec{r})$ and $\vec{a}(\vec{r})$, namely,

$$H_{\rm rad}=\frac{1}{8\pi}\int\{[4\pi c\vec{\Pi}(\vec{r})]^2+[\vec{\nabla}\times\vec{a}(\vec{r})]^2\}d\vec{r}\,. \tag{51}$$

Expressing the commutator between the vector potential and its conjugate in terms of the mode functions for the cavity as in (52),

$$[\Pi_i(\vec{r}),a_j(\vec{r}')]=-\frac{i\hbar}{V}\sum_{\lambda}f_i^{(\lambda)}(\vec{r})f_j^{(\lambda)}(\vec{r}') \tag{52}$$

and using the completeness relation for the transverse vector functions

$$\frac{1}{V}\int_V\sum_{\lambda}f_i^{(\lambda)}(\vec{r})f_j^{(\lambda)}(\vec{r}')\Pi_j(\vec{r}')d\vec{r}'=\Pi_i(\vec{r})\,, \tag{53}$$

we have

$$H_{\rm pol}=-\frac{i}{\hbar c}\int_V p_i(\vec{r})[a_i(\vec{r}),H_{\rm rad}]d\vec{r}=4\pi c\int_V\vec{p}(\vec{r})\cdot\vec{\Pi}(\vec{r})d\vec{r}\,. \tag{54}$$

This result represents the generalization of the interaction Hamiltonian used in quantum optics. Rewriting (54) in terms of the displacement field $\vec{d}^{\perp}(\vec{r})$ and using the electric dipole approximation for the polarization field $\vec{p}(\vec{r})$, we have

$$H_{\rm pol}^{(\rm ed)}=-\vec{\mu}\cdot\vec{d}^{\perp}\,. \tag{55}$$

Using (54), the last term of (50) becomes

$$-\frac{2\pi i}{\hbar}\int\int p_i(\vec{r})p_j(\vec{r}')[a_i(\vec{r}),\Pi_j(\vec{r}')]d\vec{r}d\vec{r}'\,. \tag{56}$$

For the commutator in (56) it is convenient to use the alternative form to (52), namely,

$$[\Pi_i(\vec{r}),a_j(\vec{r}')]=-ih\left[\delta_{ij}^{\perp}(\vec{r}-\vec{r}')-\frac{1}{4\pi}\nabla_i\nabla_j'\int_{\bar{V}}\frac{\tilde{\theta}(\vec{s};\vec{r}')}{|\vec{r}-\vec{s}|}d\vec{s}\right]. \tag{57}$$

Hence (56) is

$$2\pi\int_V\int_V p_i(\vec{r})p_j(\vec{r}')\left[\delta_{ij}^{\perp}(\vec{r}-\vec{r}')-\frac{1}{4\pi}\nabla_i\nabla_j'\int_{\bar{V}}\frac{\tilde{\theta}(\vec{s};\vec{r}')}{|\vec{r}-\vec{s}|}d\vec{s}\right]d\vec{r}'d\vec{r} \tag{58}$$

$$=2\pi\int_V|\vec{p}^{\perp}(\vec{r})|^2d\vec{r}+\tfrac{1}{2}\int_V\int_V\int_{\bar{V}}\frac{\vec{\nabla}\cdot\vec{p}(\vec{r})p_j(\vec{r}')\nabla_j'\tilde{\theta}(\vec{s};\vec{r}')}{|\vec{r}-\vec{s}|}d\vec{s}d\vec{r}'d\vec{r} \tag{59}$$

$$=2\pi\int_V|\vec{p}^{\perp}(\vec{r})|^2d\vec{r}-\tfrac{1}{2}\int_V\int_{\bar{V}}\frac{\rho(\vec{r})\tilde{\rho}(\vec{s})}{|\vec{r}-\vec{s}|}d\vec{s}d\vec{r}\,. \tag{60}$$

To obtain (60) from (59) we have used the relations

$$\vec{\nabla}\cdot\vec{p}(\vec{r})=-\rho(\vec{r}) \tag{61}$$

and

$$\begin{aligned}\tilde{\rho}(\vec{s})&=\int_V\rho(\vec{r}')\tilde{\theta}(\vec{s};\vec{r}')d\vec{r}'\\&=\int_V p_j(\vec{r}')\nabla_j'\tilde{\theta}(\vec{s};\vec{r}')d\vec{r}'\,.\end{aligned} \tag{62}$$

Collecting all the contributions, we have for the new Hamiltonian,

$$\begin{aligned}H=&H_{\rm atoms}+H_{\rm rad}+H_{\rm pol}+H_{\rm mag}+H_{\rm dia}\\&+V_{\rm inter}+V_{\rm image}+2\pi\int_V|\vec{p}^{\perp}(\vec{r})|^2d\vec{r}\\&-\tfrac{1}{2}\int_V\int_{\bar{V}}\frac{\rho(\vec{r})\tilde{\rho}(\vec{s})}{|\vec{r}-\vec{s}|}d\vec{s}d\vec{r}\,.\end{aligned} \tag{63}$$

The interatomic part of $2\pi\int |\vec{p}^{\perp}(\vec{r})|^2 d\vec{r}$ cancels exactly the V_{inter} term as in the conventional multipolar transformation. In addition, we now have the *exact* cancellation of the V_{image} term since the last term of (63) is the negative of the V_{image} in the original Hamiltonian. Thus the new Hamiltonian is

$$H_{\text{mult}}=H_{\text{atoms}}+H_{\text{rad}}+H_{\text{pol}}+H_{\text{mag}}+H_{\text{dia}}\ , \tag{64}$$

where H_{atoms} includes the one-center, field-independent terms. We emphasize the fact that, in contrast to the minimal-coupling Hamiltonian (34), the multipolar form (64) does not make any explicit reference to the image charges. The effect of the confinement in the cavity is completely accounted for by the use of the appropriate field modes $\vec{f}^{(\lambda)}(\vec{r})$.

V. APPLICATIONS

The simplest shape of a cavity for calculations is the rectangular parallelepiped ($x=\alpha, y=\beta, z=\gamma$), which has the mode functions

$$\begin{aligned} f_x&=\sqrt{8}e_x\cos k_x x\sin k_y y\sin k_z z\ ,\\ f_y&=\sqrt{8}e_y\sin k_x x\cos k_y y\sin k_z z\ ,\\ f_z&=\sqrt{8}e_z\sin k_x x\sin k_y y\cos k_z z\ . \end{aligned} \tag{65}$$

The unit vector $\vec{e}$, defining the field polarization, is normal to $\hat{\vec{k}}$. We consider, for the purpose of illustration, the case of atoms near one of the walls of the parallelepiped, say $z=0$, but sufficiently far away from the other walls that their effects may be ignored. It is straightforward to generalize the calculation to include these additional effects if necessary.

We give below two general relationships which are used in the calculations in this section. For $\vec{r}$ and $\vec{r}'$ near one wall but far away from others, the sum of $f_i^{(\lambda)}(\vec{r})f_j^{(\lambda)}(\vec{r}')$ for a given $\vec{k}$ is

$$\sum_{\text{pol}} f_i^{(\lambda)}(\vec{r})f_j^{(\lambda)}(\vec{r}')=(\delta_{ij}-\hat{k}_i\hat{k}_j)e^{i\vec{k}\cdot(\vec{r}-\vec{r}')} -\sigma_{il}(\delta_{lj}-\hat{k}_l\hat{k}_j)e^{i\vec{k}\cdot(\vec{r}-\sigma\vec{r}')}\ . \tag{66}$$

When the sum is carried over $\vec{k}$ as well, we have

$$\frac{1}{V}\sum_{\lambda} f_i^{(\lambda)}(\vec{r})f_j^{(\lambda)}(\vec{r}')=\delta_{ij}^{\perp}(\vec{r}-\vec{r}') -\sigma_{il}\delta_{ij}^{\perp}(\vec{r}-\sigma\vec{r}')\ . \tag{67}$$

A. An atom near a conducting wall

In his examination of the inadequacy of the two-level model for an atom interacting with radiation, Barton[3] has calculated the energy of interaction between an atom and a wall using the minimal-coupling formalism. As our first application, we consider this problem and show how the energy shift may be calculated in a simple way using the transformed multipolar Hamiltonian. In the electric dipole approximation the Hamiltonian is

$$H=H_{\text{atom}}+H_{\text{rad}}-\vec{\mu}\cdot\vec{d}^{\perp}(\vec{R})\ , \tag{68}$$

where $\vec{\mu}$ is the electric dipole moment operator and $\vec{R}$ is the position vector of the atom. The leading contribution is of second order and the energy shift of the atom in state $|r\rangle$ is

$$\Delta E_r=\sum_{s,\lambda}\frac{\langle 0,r|-\vec{\mu}\cdot\vec{d}(\vec{R})|s,1_\lambda\rangle\langle 1_\lambda,s|-\vec{\mu}\cdot\vec{d}(\vec{R})|r,0\rangle}{E_r-(E_s+\hbar ck^{(\lambda)})}\ . \tag{69}$$

The matrix elements are calculated using the mode expansion analogous to (4) with the $\vec{f}$'s given by (65). We have

$$\Delta E_r=-\frac{2\pi}{V}\sum_s \mu_i^{rs}\mu_j^{sr}\sum_{\lambda}\frac{k^{(\lambda)}}{k_{sr}+k^{(\lambda)}}f_i^{(\lambda)}(\vec{R})f_j^{(\lambda)}(\vec{R})\ , \tag{70}$$

where $\hbar ck_{sr}=E_s-E_r$. The energy shift contains the usual self-energy terms in addition to the interaction energy with the wall. Using (66) the identification is immediate: The first summand in (66) leads to the self-energy term and the second to

$$U(\vec{R})=2\pi\sum_s \mu_i^{rs}\mu_j^{sr}\sigma_{il}\int \frac{k}{k_{sr}+k}(\delta_{lj}-\hat{k}_l\hat{k}_j)e^{i\vec{k}\cdot(\vec{R}-\sigma\vec{R})}\frac{d\vec{k}}{(2\pi)^3}$$
$$=-2\pi\sum_s \tilde{\mu}_i^{rs}\mu_j^{sr}\int \frac{k}{k_{sr}+k}(\delta_{ij}-\hat{k}_i\hat{k}_j)e^{i\vec{k}\cdot\vec{Q}}\frac{d\vec{k}}{(2\pi)^3}$$
$$=\frac{1}{\pi}\sum_s \tilde{\mu}_i^{rs}\mu_j^{sr}(\delta_{ij}\nabla^2-\nabla_i\nabla_j)\left[\frac{f(k_{sr}Q)}{Q}\right], \tag{71}$$

where $\vec{Q}=(\vec{R}-\sigma\vec{R})$ and the gradients are with respect to $\vec{Q}$. We note that $Q=|\vec{Q}|=2L$, where L is the shortest distance to the wall $z=0$, and the direction of $\vec{Q}$ is $\hat{\vec{n}}$ normal to the wall. For $k_{sr}>0$, as for example when $|r\rangle$ is the ground state of the atom, the interaction energy (71) becomes

$$U(L)=\frac{1}{\pi}\sum_s \frac{\tilde{\mu}_i^{rs}\mu_j^{sr}}{(2L)^3}\{(\delta_{ij}-3\hat{n}_i\hat{n}_j)[f(2k_{sr}L)+(2k_{sr}L)g(2k_{sr}L)]+(\delta_{ij}-\hat{n}_i\hat{n}_j)[2k_{sr}L-(2k_{sr}L)^2f(2k_{sr}L)]\}, \tag{72}$$

where

$$f(z)=\mathrm{Ci}(z)\sin z-\mathrm{si}(z)\cos z,$$
$$g(z)=-\mathrm{Ci}(z)\cos z-\mathrm{si}(z)\sin z, \quad z>0 \tag{73}$$

We note that in the near-zone limit, i.e., for $k_{sr}L<<1$, $f(z)\to\pi/2$, and $g(z)\to\ln z$, so that as expected

$$U(L)\to\tfrac{1}{2}\sum_s \frac{\tilde{\mu}_i^{rs}\mu_j^{sr}}{(2L)^3}(\delta_{ij}-3\hat{n}_i\hat{n}_j). \tag{74}$$

On the other hand, in the far-zone limit $k_{sr}L>>1$,

$$U(L)\to\frac{4}{\pi}\sum \frac{\tilde{\mu}_i^{rs}\mu_j^{sr}}{k_{sr}(2L)^4}(\delta_{ij}-2\hat{n}_i\hat{n}_j). \tag{75}$$

In terms of the electric dipole polarizability (76) of the atom,

$$\alpha=\tfrac{2}{3}\sum_s \frac{|\vec{\mu}^{rs}|^2}{E_{sr}}. \tag{76}$$

This limit becomes the known result,[8]

$$U(L)=-\left[\frac{3\hbar c}{8\pi}\right]\frac{\alpha}{L^4}. \tag{77}$$

When the atom is in an excited state, some of the virtual transitions are downwards and the corresponding k_{sr}'s are negative. For such a case, the sum over s in the energy expression may be divided into two parts: one with $k_{sr}>0$, giving results as above, and the other with $k_{sr}<0$. The latter contribution is

$$2\pi\sum_{s(k_{sr}<0)} \tilde{\mu}_i^{rs}\mu_j^{sr}(\delta_{ij}\nabla^2-\nabla_i\nabla_j)\int \frac{ke^{i\vec{k}\cdot\vec{Q}}}{(k-|k_{sr}|)}\frac{dk\,d\Omega}{(2\pi)^3} \tag{78}$$
$$=-\frac{1}{\pi}\sum_{s(k_{sr}<0)} \tilde{\mu}_i^{rs}\mu_j^{sr}(\delta_{ij}\nabla^2-\nabla_i\nabla_j)\left[\frac{f(|k_{sr}|Q)}{Q}-\pi\frac{\cos(|k_{sr}|Q)}{Q}\right] \tag{79}$$
$$=-\frac{1}{\pi}\sum_{s(k_{sr}<0)} \frac{\tilde{\mu}_i^{rs}\mu_j^{sr}}{(2L)^3}\{(\delta_{ij}-3\hat{n}_i\hat{n}_j)[f(2|k_{sr}|L)+2|k_{sr}|Lg(2|k_{sr}|L)]$$
$$+(\delta_{ij}-\hat{n}_i\hat{n}_j)[2|k_{sr}|L-(2|k_{sr}|L)^2f(2|k_{sr}|L)]\}$$
$$+\sum_{s(k_{sr}<0)} \frac{\tilde{\mu}_i^{rs}\mu_j^{sr}}{(2L)^3}\{(\delta_{ij}-3\hat{n}_i\hat{n}_j)[\cos(2|k_{sr}|L)+(2|k_{sr}|L)\sin(2|k_{sr}|L)]$$
$$+(\delta_{ij}-\hat{n}_i\hat{n}_j)[(2|k_{sr}|L)^2\cos(2|k_{sr}|L)]\}. \tag{80}$$

The modulating term, the second summand of (80), may be interpreted as the retarded resonance interaction between the transition dipoles and their images.

B. A pair of atoms near a conducting wall: effect on the interatomic potential

In addition to the attractions calculated in the previous subsection, there are interatomic effects due to the presence of a metal surface near a pair of atoms. We evaluate these energies when the atoms are in their ground states and compare them with the well-known London and Casimir-Polder potentials. As before, we employ the electric dipole approximation and use the Hamiltonian

$$H=H_A+H_B+H_{\rm rad}-\vec{\mu}(A)\cdot\vec{d}^{\perp}(\vec{R}_A)-\vec{\mu}(B)\cdot\vec{d}^{\perp}(\vec{R}_B)\ , \tag{81}$$

where $\vec{R}_A$ and $\vec{R}_B$ are the position vectors of the atoms A and B.

The energy shift due to the coupling of the atom to the electromagnetic field is evaluated correct to fourth order in a manner similar to that used for retarded dispersion interactions. From the graphs shown in Fig. 1 and their reflections, we obtain

$$\Delta E=\sum_{r,s}\mu_i^{or}(A)\mu_j^{ro}(A)\mu_k^{os}(B)\mu_l^{so}(B)$$
$$\times\frac{1}{V^2}\sum_{\lambda,\lambda';a}\frac{(2\pi\hbar cp^{(\lambda)})(2\pi\hbar cp^{(\lambda')})}{D_a^{\lambda\lambda'}}f_i^{(\lambda)}(\vec{R}_A)f_j^{(\lambda)}(\vec{R}_A)f_k^{(\lambda)}(\vec{R}_B)f_l^{(\lambda)}(\vec{R}_B)\ , \tag{82}$$

where D_a's are the appropriate energy denominators. For example,

$$D_i=-(E_{ro}^A+\hbar cp)(E_{so}^B+\hbar cp')(\hbar cp+\hbar cp')\ . \tag{83}$$

We confine our calculations to two regions of physical interest, namely, the near-zone (London) and the far-zone (Casimir) limits. In these limits the calculations are considerably simpler than the general case because the energy denominators can be approximated as follows. In the near-zone, the dominant contributions arise when $p,p'>>k_{ro},k_{so}$; it is therefore sufficient to consider graphs (iii) and (iv) of Fig. 1 and their reflections. For these graphs the denominator is $-\hbar cp\hbar cp'(\hbar ck_{ro}+\hbar ck_{so})$. In the far-zone, $p,p'<<k_{ro},k_{so}$ and graphs (i), (ii), and their reflections make the dominant contributions; for these graphs the energy denominator is $-\hbar ck_{ro}\hbar ck_{so}(\hbar cp+\hbar cp')$.

We first consider the near-zone limit for which the energy shift is

$$E\approx-16\pi^2\sum_{r,s}\frac{\mu_i^{or}(A)\mu_j^{ro}(A)\mu_k^{os}(B)\mu_l^{so}(B)}{(E_{ro}^A+E_{so}^B)}$$
$$\times\frac{1}{V^2}\sum_{\lambda}f_i^{(\lambda)}(\vec{R}_A)f_k^{(\lambda)}(\vec{R}_B)\sum_{\lambda}f_j^{(\lambda')}(\vec{R}_A)f_l^{(\lambda')}(\vec{R}_B)$$
$$=-16\pi^2\sum_{r,s}\frac{\mu_i^{or}(A)\mu_j^{ro}(A)\mu_k^{os}(B)\mu_l^{so}(B)}{(E_{ro}^A+E_{so}^B)}$$
$$\times[\delta_{ik}^{\perp}(\vec{R})-\sigma_{im}\delta_{mk}^{\perp}(\bar{\bar{R}})][\delta_{jl}^{\perp}(\vec{R})-\sigma_{jn}\delta_{nl}^{\perp}(\bar{\bar{R}})]\ , \tag{84}$$

where (67) has been used for the sum over the modes; also $\vec{R}=\vec{R}_B-\vec{R}_A$ and $\bar{\bar{R}}=\vec{R}_B-\tilde{\tilde{R}}_A$. The term depending only on $\vec{R}$ is

$$-\sum_{r,s}\frac{\mu_i^{or}(A)\mu_j^{ro}(A)\mu_k^{os}(B)\mu_l^{so}(B)}{(E_{ro}^A+E_{so}^B)}\frac{(\delta_{ik}-3\hat{R}_i\hat{R}_k)(\delta_{jl}-3\hat{R}_j\hat{R}_l)}{R^6}\ , \tag{85}$$

which may be written in terms of atomic polarizabilities (76) as

$$-\frac{1}{4}\frac{\alpha(A)\alpha(B)}{R^6}\sum_{r,s}\frac{E^A_{ro}E^B_{so}}{(E^A_{ro}+E^B_{so})}\delta_{ij}\delta_{kl}(\delta_{ik}-3\hat{R}_i\hat{R}_k)(\delta_{jl}-3\hat{R}_j\hat{R}_l)\ . \tag{86}$$

Defining an average transition energy

$$\bar{E}=2\sum_{r,s}\frac{E^A_{ro}E^B_{so}}{(E^A_{ro}+E^B_{so})}\ , \tag{87}$$

we obtain the London dispersion potential between the atoms:

$$U_{\text{London}}(R)=-\frac{3}{4}\bar{E}\frac{\alpha(A)\alpha(B)}{R^6}\ . \tag{88}$$

The term depending only on $\bar{R}$ is $U_{\text{London}}(\bar{R})$. The remaining terms depending on both R and $\bar{R}$ are summed to give

$$2\sum_{r,s}\frac{\mu_i^{or}(A)\mu_j^{ro}(A)\mu_k^{os}(B)\mu_l^{so}(B)}{(E^A_{ro}+E^B_{so})}\frac{(\delta_{ik}-3\hat{R}_i\hat{R}_k)\sigma_{jn}(\delta_{nl}-3\hat{\bar{R}}_n\hat{\bar{R}}_l)}{R^3\bar{R}^3}\ , \tag{89}$$

which, in terms of the atomic polarizabilities and $\bar{E}$, is

$$U_{\text{London}}(R,\bar{R})=\bar{E}\frac{\alpha(A)\alpha(B)}{4R^3\bar{R}^3}\delta_{ij}\delta_{kl}(\delta_{ik}-3\hat{R}_i\hat{R}_k)\sigma_{jn}(\delta_{nl}-3\hat{\bar{R}}_n\hat{\bar{R}}_l)$$

$$=\bar{E}\frac{\alpha(A)\alpha(B)}{4R^3\bar{R}^3}(3\sin^2\epsilon+3\sin^2\bar{\epsilon}-2)\ , \tag{90}$$

where ϵ and $\bar{\epsilon}$ are the angles that $\vec{\mathrm{R}}$ and $\vec{\bar{\mathrm{R}}}$ make with $\hat{\mathrm{n}}$.

In the far zone, where R is larger than transition wavelengths, the energy shift is

$$\Delta E\approx-16\pi^2\hbar c\sum_{r,s}\frac{\mu_i^{or}(A)\mu_j^{ro}(A)\mu_k^{os}(B)\mu_l^{so}(B)}{E^A_{ro}E^B_{so}}$$

$$\times\frac{1}{V^2}\sum_{\lambda,\lambda'}pp'\frac{f_i^{(\lambda)}(\vec{\mathrm{R}}_A)f_k^{(\lambda)}(\vec{\mathrm{R}}_B)f_j^{(\lambda')}(A)f_l^{(\lambda')}(\vec{\mathrm{R}}_B)}{(p+p')}\ . \tag{91}$$

Using (76) for the atomic polarizabilities and (66) for sum over the field polarization directions, (91) becomes

$$\Delta E=-4\pi^2\hbar c\alpha(A)\alpha(B)\int\int\frac{pp'}{p+p'}[(\delta_{ik}-\hat{p}_i\hat{p}_k)e^{i\vec{\mathrm{p}}\cdot\vec{\mathrm{R}}}-\sigma_{im}(\delta_{mk}-\hat{p}_m\hat{p}_k)e^{i\vec{\mathrm{p}}\cdot\vec{\bar{\mathrm{R}}}}]$$

$$\times[(\delta_{ik}-\hat{p}'_i\hat{p}'_k)e^{i\vec{\mathrm{p}}'\cdot\vec{\mathrm{R}}}$$

$$-\sigma_{in}(\delta_{nk}-\hat{p}'_n\hat{p}'_k)e^{i\vec{\mathrm{p}}'\cdot\vec{\bar{\mathrm{R}}}}]\frac{d\vec{\mathrm{p}}d\vec{\mathrm{p}}'}{(2\pi)^6}\ . \tag{92}$$

The term depending only on R is the Casimir asymptotic potential

$$U_{\text{Casimir}}=-\frac{23}{4\pi}\hbar c\frac{\alpha(A)\alpha(B)}{R^7}\ . \tag{93}$$

Similarly, the term depending only on $\bar{R}$ is $U_{\text{Casimir}}(\bar{R})$. The $R\bar{R}$-dependent term may be written as

$$\frac{1}{8\pi^4}\hbar c\alpha(A)\alpha(B)\sigma_{mn}(\delta_{mk}\nabla^2-\nabla_m\nabla_k)(\delta_{nk}\bar{\nabla}^2-\bar{\nabla}_n\bar{\nabla}_k)\int\frac{pp'}{p+p'}e^{i\vec{\mathrm{p}}\cdot\vec{\bar{\mathrm{R}}}}dp\,dp'd\Omega\,d\Omega'$$

$$=\frac{\hbar c}{\pi}\alpha(A)\alpha(B)\sigma_{mn}(\delta_{mk}\nabla^2-\nabla_m\nabla_k)(\delta_{nk}\bar{\nabla}^2-\bar{\nabla}_n\bar{\nabla}_k)\frac{1}{R\bar{R}(R+\bar{R})}\ , \tag{94}$$

which, after straightforward differentiation, gives

$$U_{\text{Casimir}}(R,\bar{R})=\frac{8}{\pi}\hbar c\frac{\alpha(A)\alpha(B)}{R^3\bar{R}^3(R+\bar{R})^5}[R^4\sin^2\epsilon+5R^3\bar{R}\sin^2\bar{\epsilon}$$
$$+R^2\bar{R}^2(6+\sin^2\epsilon+\sin^2\bar{\epsilon})+5R\bar{R}^3\sin^2\bar{\epsilon}+\bar{R}^4\sin^2\bar{\epsilon}] . \quad (95)$$

We note that when the interatomic separation vector is normal to the plane this simplifies to

$$\frac{48}{\pi}\hbar c\frac{\alpha(A)\alpha(B)}{R\bar{R}(R+\bar{R})^5} . \quad (96)$$

These potential energies depending both on R and $\bar{R}$ are a consequence of the interactions between the fluctuating dipoles of one atom with those of the other as well as with the induced fluctuating currents in the conducting plane.

C. Spontaneous emission by an excited atom in the presence of a conducting wall

In the previous applications we have calculated the effects of a conducting wall on energy shifts. We now consider a different type of process, namely, spontaneous emission. The matrix element for emission from an atom in state $|m\rangle$, using $-\vec{\mu}\cdot\vec{d}^{\perp}(\vec{R})$, is

$$M_{fi}=\left[\frac{2\pi\hbar ck}{V}\right]^{1/2}\mu_i^{mo}f_i^{(\lambda)}(\vec{R}) , \quad (97)$$

which when used in the Fermi golden rule gives for the total rate

$$\Gamma=\frac{\mu_i^{mo}\mu_j^{mo}\omega^3}{2\pi\hbar c^3}\int\sum_{\text{pol}}f_i^{(\lambda)}(\vec{R})f_j^{(\lambda)}(\vec{R})d\Omega . \quad (98)$$

In (98), $\omega(=E_{mo}/\hbar)$ is the circular frequency of the emitted light. Using (66) for the sum over polarizations, we get

$$\Gamma=\frac{\mu_i^{mo}\mu_j^{mo}\omega^3}{2\pi\hbar c^3}\left[\int(\delta_{ij}-\hat{k}_i\hat{k}_j)d\Omega-\sigma_{il}\int(\delta_{lj}-\hat{k}_l\hat{k}_j)e^{i\vec{k}\cdot(\vec{R}-\sigma\vec{R})}d\Omega\right] \quad (99)$$

$$=\frac{4|\vec{\mu}^{mo}|^2\omega^3}{3\hbar c^3}-\frac{\mu_i^{mo}\mu_j^{mo}\omega^3}{2\pi\hbar c^3}\sigma_{il}\int(\delta_{lj}-\hat{k}_l\hat{k}_j)e^{2i\vec{k}\cdot\hat{n}L}d\Omega . \quad (100)$$

The first term is the Einstein A coefficient and the second represents the effect of the wall. This term is

$$\frac{2}{\hbar c^3}|\vec{\mu}|^2\omega^3\left[\frac{\sin 2kL}{(2kL)^3}-\frac{\cos 2kL}{(2kL)^2}-\frac{\sin 2kL}{(2kL)}\right]$$
$$+\frac{2}{\hbar c^3}|\vec{\mu}\cdot\hat{\hat{n}}|^2\omega^3\left[\frac{\sin 2kL}{(2kL)^3}-\frac{\cos 2kL}{(2kL)^2}-\frac{\sin 2kL}{(2kL)}\right] . \quad (101)$$

In the near zone this is

$$-\frac{4|\vec{\mu}|^2\omega^3}{3\hbar c^3}+\frac{8|\vec{\mu}\cdot\hat{\hat{n}}|^2\omega^3}{3\hbar c^3} , \quad (102)$$

which, for a randomly oriented dipole, is $-A/3$ so that the total rate is

$$\Gamma=\tfrac{2}{3}A . \quad (103)$$

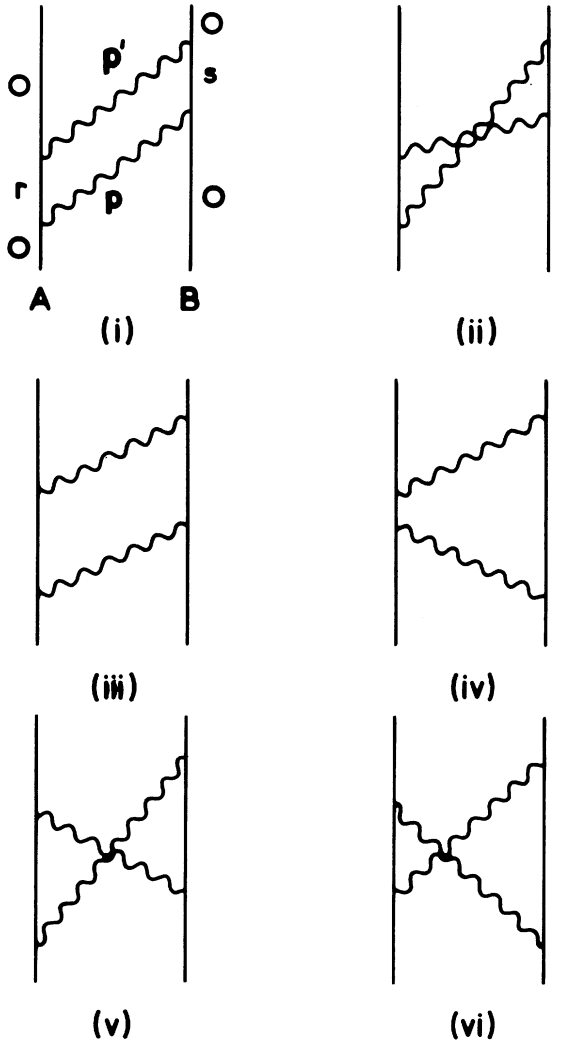

FIG. 1. Time-ordered graphs for dispersion interaction.

On the other hand, for an oriented dipole two special orientations are of interest, namely when the dipole is parallel or normal to the wall. The rates are

$$\Gamma=0\ ,$$
$$\Gamma=2A\ . \tag{104}$$

When the dipole is normal to the wall, the dipole and its image form a Dicke pair so that the emission rate is doubled; when the dipole is parallel to the wall it is out of phase with its image so that the emission is forbidden. As the distance L increases, these selection rules are weakened and in the far-zone limit the rate becomes, as expected, the Einstein rate.

VI. CONCLUSION

We have shown how the standard procedure for obtaining the multipolar Hamiltonian from the minimal-coupling form can be extended to systems confined in a cavity. In addition to the well-known cancellation of the interatomic Coulomb interactions which occur as a result of the transformation, the Coulomb image energies that are present in the minimal-coupling Hamiltonian are also eliminated completely. The interaction terms in the resultant Hamiltonian are all one center in character; interactions between atoms are mediated by transverse photon exchange. The applications given in this paper demonstrate the versatility of the new Hamiltonian.

[1]E. A. Power and S. Zienau, Philos. Trans. R. Soc. London A251, 427 (1959).
[2]M. Babiker, E. A. Power, and T. Thirunamachandran, Proc. R. Soc. London A338, 235 (1974).
[3]G. Barton, J. Phys. B 7, 2134 (1974).
[4]P. W. Milonni, Phys. Rev. A (in press).
[5]J. E. Lennard-Jones, Trans. Faraday Soc. 28, 334 (1932).
[6]J. Bardeen, Phys. Rev. 58, 727 (1940).
[7]E. A. Power and T. Thirunamachandran, Proc. R. Soc. London A372, 265 (1980).
[8]E. A. Power, *Introductory Quantum Electrodynamics* (Longmans, London, 1964).