

Quantum electrodynamics with nonrelativistic sources. I. Transformation to the multipolar formalism for second-quantized electron and Maxwell interacting fields

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The multipolar formalism is commonly used as the starting point in chemical physics and quantum optics for discussion of the interaction of radiation with atoms and molecules. The relationship of the multipolar to the minimal-coupling formalism is examined when both the electron and the radiation are second-quantized fields. Both the Lagrangian and Hamiltonian formulations are considered: in the former the transformation between the two is a point transformation on the electron field coordinates, while in the latter it is a canonical transformation. The resulting equations of motion are Maxwell's equations, in terms of the basic and auxiliary fields, for the electromagnetic field and Schrödinger equations for charges in an electromagnetic field with the coupling given through the multipole moments. That the Schrödinger equation is different from that which arises in the minimal-coupling formalism is a natural consequence of the use of new field coordinates. The theory is extended to a system of molecules anticipating the discussion of intermolecular energies in paper III (the second succeeding paper).

I. INTRODUCTION

Modern quantum optics and many applications in chemical physics that involve the interaction of radiation with atoms and molecules require, for their theoretical development, the framework of quantum electrodynamics.¹ The essential feature of the theory is that the radiation field is quantized and forms part of the dynamical system. The minimal-coupling form of the theory, although a direct consequence of relativistic quantum electrodynamics, is not well suited for these studies where bound systems are usually the sources of the electromagnetic field. Where atoms and molecules are the current sources, it is most convenient to express the interaction between them and the radiation in terms of electric and magnetic multipole moments. For this purpose, the multipolar form of the theory is the natural starting point. In this series of papers, we develop the multipolar theory from both Lagrangian and Hamiltonian points of view, and discuss several applications using this formalism in the Heisenberg picture. The time development of the field operators is used in a direct manner in these applications: This gives additional physical insight into these processes.

In this paper (paper I of the series), we first develop the multipolar theory from minimal-coupling electrodynamics. There have been several investigations²⁻⁶ concerning the relationship between these theories, and in most studies the charges were treated within the framework of first quantization. However, in the present work, the electron field, in addition to the radiation field, is second quantized. The theoretical development begins with the Lagrangian formulation. In contrast to the charged-particle-electromagnetic-field Lagrangian where the equations of motion for the charges are given by the Lorentz force in Newton's equations, now the electron fields have Schrödinger's equations in the presence of the electromagnetic field for their equations of motion. The

electromagnetic fields themselves obey Maxwell's equations in both cases, the only difference being that the localized current densities in the particle case are replaced by nonlocalized Schrödinger current densities in the present treatment.

In the charged-particle-electromagnetic-field theory the transformation from the minimal to the multipolar form may be effected by the addition of a total time derivative and does not involve any change in the electron coordinates and the vector potential. The transformation to be described in Sec. II is not effected by adding a total time derivative but by a change in the generalized coordinates which are the electron fields. Because of this, the Schrödinger equations for the electron fields are different in the two formulations. In Sec. III the minimal and multipolar Hamiltonians are obtained and their significant differences are discussed. The two Hamiltonians are related in the quantum theory by a canonical transformation which is described in Sec. IV. This transformation is in fact a generalization of the previous approaches and this allows a direct comparison between the new and old Schrödinger-type equations. In Sec. V we extend the multipolar theory to molecular assemblies. This extension is essential for studies of intermolecular interactions and the interaction of radiation with such assemblies. A striking feature of this formalism is that the intermolecular electrostatic terms in the Hamiltonian are eliminated in favor of couplings via the exchange of transverse photons.^{2,7,8}

The multipolar formalism developed in this paper is used in papers II and III to study one-center radiation problems and intermolecular forces, respectively. The role that the time-dependent electromagnetic fields takes in these applications is examined in detail. An interesting finding is that it is important to go beyond the quantum analogs of the classical fields that are linearly dependent on the multipolar sources. These applications in fact demonstrate the necessity of including the electromagnetic fields that are nonlinear in the source strengths.

II. MINIMAL-COUPLING LAGRANGIAN AND TRANSFORMATION TO THE MULTIPOLAR FORM

A. Minimal-coupling Lagrangian and equations of motion

It is well known⁹ that the Lagrangian for an electron field uncoupled from the radiation field is

$$L_{\text{charge}} = - \int \bar{\psi}(\vec{q}) \left[-\frac{\hbar^2}{2m} (\nabla^{(q)})^2 + V(\vec{q}) \right] \psi(\vec{q}) d^3q + \frac{i\hbar}{2} \int [\bar{\psi}(\vec{q})\dot{\psi}(\vec{q}) - \dot{\bar{\psi}}(\vec{q})\psi(\vec{q})] d^3q. \quad (2.1)$$

In (2.1), $V(\vec{q})$ is the potential due to external sources such

$$L_{\text{min}}(\vec{a}^\perp, \psi, \bar{\psi}; \dot{\vec{a}}^\perp, \dot{\psi}, \dot{\bar{\psi}}) = \int \mathcal{L}_{\text{min}} dV = - \int \bar{\psi}(\vec{q}) \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{e}{c} \vec{a}^\perp(\vec{q}) \right]^2 + V(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\psi}(\vec{q}')\psi(\vec{q}')}{|\vec{q}-\vec{q}'|} d^3q' \right] \psi(\vec{q}) d^3q + \frac{i\hbar}{2} \int [\bar{\psi}(\vec{q})\dot{\psi}(\vec{q}) - \dot{\bar{\psi}}(\vec{q})\psi(\vec{q})] d^3q + \frac{1}{8\pi} \int \{ [\dot{\vec{a}}^\perp(\vec{r})/c]^2 - [\text{curl} \vec{a}^\perp(\vec{r})]^2 \} d^3r. \quad (2.3)$$

From (2.3) the equations of motion for the system are easily derived. The variation with respect to $\vec{a}^\perp(\vec{r})$ gives

$$\frac{\partial}{\partial t} \frac{\partial \mathcal{L}_{\text{min}}}{\partial \dot{a}_i^\perp} + \frac{\partial}{\partial x_j} \frac{\partial \mathcal{L}_{\text{min}}}{\partial (\partial a_i^\perp / \partial x_j)} - \frac{\partial \mathcal{L}_{\text{min}}}{\partial a_i^\perp} = 0 \quad (2.4)$$

which leads to

$$\frac{\ddot{a}_i^\perp(\vec{r})}{c^2} - [\text{curl} \text{curl} \vec{a}^\perp(\vec{r})]_i + \frac{4\pi e}{mc} \int \bar{\psi}(\vec{q}) \left[-i\hbar \vec{\nabla}^{(q)} + \frac{e}{c} \vec{a}^\perp(\vec{q}) \right]_j \delta_{ij}^{\perp}(\vec{r}-\vec{q}) \psi(\vec{q}) d^3q = 0. \quad (2.5)$$

In terms of the transverse electric field $\vec{e}^\perp(\vec{r}) = -\dot{\vec{a}}^\perp(\vec{r})/c$ and the magnetic field $\vec{b}(\vec{r}) = \text{curl} \vec{a}^\perp(\vec{r})$, Eq. (2.5) is

$$\text{curl} \vec{b}(\vec{r}) = \frac{1}{c} \frac{\partial \vec{e}^\perp(\vec{r})}{\partial t} + \frac{4\pi}{c} \vec{j}^\perp(\vec{r}), \quad (2.6)$$

where

$$\vec{j}_i^\perp(\vec{r}) = -e \int \bar{\psi}(\vec{q}) \left[-i\hbar \vec{\nabla}^{(q)} + \frac{e}{c} \vec{a}^\perp(\vec{q}) \right]_j \times \delta_{ij}^{\perp}(\vec{r}-\vec{q}) \psi(\vec{q}) d^3q. \quad (2.7)$$

Equation (2.6) is the transverse part of the Maxwell equation for $\text{curl} \vec{b}(\vec{r})$. The equation for the electron field $\psi(\vec{q})$, the analog of (2.2), is found to be

$$i\hbar \dot{\psi}(\vec{q}) = \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{e}{c} \vec{a}^\perp(\vec{q}) \right]^2 + V(\vec{q}) + e^2 \int \frac{\bar{\psi}(\vec{q}')\psi(\vec{q}')}{|\vec{q}-\vec{q}'|} d^3q' \right] \psi(\vec{q}). \quad (2.8)$$

as a nucleus, and self-interaction energies have been ignored. The Euler-Lagrange equations for $\bar{\psi}$ and ψ obtained by variation of (2.1) are the Schrödinger equation (2.2) and its complex conjugate,

$$i\hbar \dot{\bar{\psi}}(\vec{q}) = \left[-\frac{\hbar^2}{2m} (\nabla^{(q)})^2 + V(\vec{q}) \right] \bar{\psi}(\vec{q}). \quad (2.2)$$

The minimal-coupling prescription for taking into account the interaction of the electron field (charge $-e$) with the transverse electromagnetic field is to replace $-i\hbar \vec{\nabla}^{(q)}$ by $-i\hbar \vec{\nabla}^{(q)} + (e/c) \vec{a}^\perp(\vec{q})$. Also, for consistency, when the electron-radiation interaction is included, it is necessary to have the self-interaction energy in addition to the external potential energy. Thus the minimal-coupling Lagrangian for the system is

B. The multipolar Hamiltonian

The multipolar formalism is related to the above through a change of the generalized coordinates describing the system. Although the electromagnetic field coordinate $\vec{a}^\perp(\vec{r})$, the vector potential, is unchanged, the one describing the electron field is transformed according to

$$\psi(\vec{q}) = e^{-iS(\vec{q})} \phi(\vec{q}), \quad (2.9)$$

where $S(\vec{q})$ is given by

$$S(\vec{q}) = \frac{1}{\hbar c} \int \vec{p}(\vec{r}, \vec{q}) \cdot \vec{a}^\perp(\vec{r}) d^3r. \quad (2.10)$$

In Eq. (2.10), $\vec{p}(\vec{r}, \vec{q})$ is the polarization vector field. For bound electrons in an atom or molecule, the polarization field is localized and is conveniently expressed as a multipolar expansion about a fixed point such as the inversion center for a centrosymmetric molecule. For large molecules with several chromophores, it is physically realistic to localize the polarization field at the centers of the chromophores. Here the theory is developed for a small molecule or a single chromophore located at a fixed \vec{R} . The many-center theory is given in Sec. V. For one center, the

polarization field is

$$\vec{p}(\vec{r}, \vec{q}) = \vec{\mu} \delta(\vec{r} - \vec{R}) - \vec{Q} \cdot \vec{\nabla} \delta(\vec{r} - \vec{R}) + \dots, \quad (2.11)$$

where $\vec{\mu}$ and \vec{Q} are the electric dipole and quadrupole moments,

$$\vec{\mu} = -e(\vec{q} - \vec{R}), \quad \vec{Q} = -\frac{e}{2}(\vec{q} - \vec{R})(\vec{q} - \vec{R}). \quad (2.12)$$

The multipolar Lagrangian is obtained from the minimal-coupling Lagrangian (2.3) using the coordinate transformation (2.9),

$$\begin{aligned} L_{\min}(\vec{a}^\perp, \psi, \bar{\psi}; \dot{\vec{a}}^\perp, \dot{\psi}, \dot{\bar{\psi}}) &= L_{\min} \left[\vec{a}^\perp, e^{iS} \phi, \bar{\phi} e^{-iS}, \dot{\vec{a}}^\perp, \frac{d}{dt}(e^{iS} \phi), \frac{d}{dt}(\bar{\phi} e^{-iS}) \right] \\ &= L_{\text{mult}}(\vec{a}^\perp, \phi, \bar{\phi}; \dot{\vec{a}}^\perp, \dot{\phi}, \dot{\bar{\phi}}). \end{aligned} \quad (2.13)$$

Thus

$$\begin{aligned} L_{\text{mult}} &= -\int \bar{\phi}(\vec{q}) e^{-iS} \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{e}{c} \vec{a}^\perp(\vec{q}) \right]^2 + V(\vec{q}) + \frac{e^2}{2} \int \frac{\phi(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] e^{iS} \phi(\vec{q}) d^3q \\ &\quad + \frac{i\hbar}{2} \int \left[\bar{\phi}(\vec{q}) e^{-iS} \frac{d}{dt} [e^{iS} \phi(\vec{q})] - \frac{d}{dt} [\bar{\phi}(\vec{q}) e^{-iS}] e^{iS} \phi(\vec{q}) \right] d^3q + \frac{1}{8\pi} \int \left[\left[\frac{\dot{\vec{a}}^\perp(\vec{r})}{c} \right]^2 - [\text{curl} \vec{a}(\vec{r})]^2 \right] d^3r \\ &= -\int \bar{\phi}(\vec{q}) \left\{ \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{e}{c} \vec{a}^\perp(\vec{q}) \right] + \hbar \vec{\nabla}^{(q)} S(\vec{q}) \right]^2 + V(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right\} \phi(\vec{q}) d^3q \\ &\quad + \frac{i\hbar}{2} \int [\phi(\vec{q}) \dot{\phi}(\vec{q}) - \dot{\bar{\phi}}(\vec{q}) \phi(\vec{q})] d^3q - \frac{1}{c} \int \int \bar{\phi}(\vec{q}) \vec{p}(\vec{r}, \vec{q}) \cdot \dot{\vec{a}}^\perp(\vec{r}) \phi(\vec{q}) d^3r d^3q \\ &\quad + \frac{1}{8\pi} \int \left[\left[\frac{\dot{\vec{a}}^\perp(\vec{r})}{c} \right]^2 - [\text{curl} \vec{a}(\vec{r})]^2 \right] d^3r = \int \mathcal{L}_{\text{mult}} dV. \end{aligned} \quad (2.14)$$

Before considering the complete Lagrangian (2.14), we examine its form for a bound system in the low multipole order approximation. First, with the *electric dipole* contributions alone, the spatial variation of the vector potential over the molecule is ignored; $\vec{a}^\perp(\vec{q})$ is assigned the value $\vec{a}^\perp(\vec{R})$ and it is evident that only the dipole term of the polarization field (2.11) contributes. Within this approximation,

$$\frac{e}{c} \vec{a}^\perp(\vec{q}) + \hbar \vec{\nabla}^{(q)} S(\vec{q}) \simeq \frac{e}{c} \vec{a}^\perp(\vec{R}) - \frac{e}{c} \vec{\nabla}^{(q)} \int (\vec{q} - \vec{R}) \cdot \vec{a}^\perp(\vec{R}) \delta(\vec{r} - \vec{R}) d^3r = 0. \quad (2.15)$$

Thus

$$\begin{aligned} L_{\text{mult}} &= -\int \bar{\phi}(\vec{q}) \left\{ -\frac{\hbar^2}{2m} (\nabla^{(q)})^2 + V(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right\} \phi(\vec{q}) d^3q \\ &\quad + \frac{i\hbar}{2} \int [\bar{\phi}(\vec{q}) \dot{\phi}(\vec{q}) - \dot{\bar{\phi}}(\vec{q}) \phi(\vec{q})] d^3q + \frac{e}{c} \int \bar{\phi}(\vec{q}) (\vec{q} - \vec{R}) \cdot \dot{\vec{a}}^\perp(\vec{R}) \phi(\vec{q}) d^3q \\ &\quad + \frac{1}{8\pi} \int \left[\left[\frac{\dot{\vec{a}}^\perp(\vec{r})}{c} \right]^2 - [\text{curl} \vec{a}(\vec{r})]^2 \right] d^3r. \end{aligned} \quad (2.16)$$

When the electric dipole approximation is relaxed, the cancellation that is shown in (2.15) no longer occurs. For example, by retaining the electric quadrupole contribution to the polarization field and the first spatial derivative of the vector potential, we have

$$\begin{aligned} \frac{e}{c} a_i^\perp(\vec{q}) + \hbar \nabla_i^{(q)} S(\vec{q}) &\simeq \frac{e}{c} (\vec{q} - \vec{R})_j \nabla_j a_i^\perp(\vec{R}) - \frac{e}{2c} \nabla_i^{(q)} [(\vec{q} - \vec{R})_k (\vec{q} - \vec{R})_j \nabla_k a_j^\perp(\vec{R})] \\ &= \frac{e}{2c} (\vec{q} - \vec{R})_j [\nabla_j a_i^\perp(\vec{R}) - \nabla_i a_j^\perp(\vec{R})] \\ &= -\frac{e}{2c} [(\vec{q} - \vec{R}) \times \vec{b}(\vec{R})]_i. \end{aligned} \quad (2.17)$$

If (2.17) is used in the Lagrangian (2.14) together with the quadrupole contributions in the $\vec{p} \cdot \dot{\vec{a}}$ term, the multipolar Lagrangian in this higher approximation becomes

$$\begin{aligned}
L_{\text{mult}} = & - \int \bar{\phi}(\bar{q}) \left[\frac{1}{2m} \left[-i\hbar \bar{\nabla}^{(q)} - \frac{e}{2c} [(\bar{q} - \bar{\mathbf{R}}) \times \bar{\mathbf{b}}(\bar{\mathbf{R}})] \right]^2 + V(\bar{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}(\bar{q}') \phi(\bar{q}')}{|\bar{q} - \bar{q}'|} d^3 q' \right] \phi(\bar{q}) d^3 q \\
& + \frac{i\hbar}{2} \int [\bar{\phi}(\bar{q}) \dot{\phi}(\bar{q}) - \dot{\bar{\phi}}(\bar{q}) \phi(\bar{q})] d^3 q + \frac{e}{c} \int \bar{\phi}(\bar{q}) (\bar{q} - \bar{\mathbf{R}}) \cdot \dot{\bar{\mathbf{a}}}^{\perp}(\bar{\mathbf{R}}) \phi(\bar{q}) d^3 q + \frac{1}{8\pi} \int \left[\left(\frac{\dot{\bar{\mathbf{a}}}^{\perp}}{c} \right)^2 - [\text{curl} \bar{\mathbf{a}}(\bar{\mathbf{r}})]^2 \right] d^3 r .
\end{aligned} \tag{2.18}$$

We remark that the electric quadrupole and magnetic dipole interactions are of the same order and the approximation (2.18) contains the magnetic dipole interaction in the cross term of the first integral in L_{mult} .

The above discussion is easily generalized by using the complete multipolar expansion for the electric polarization field of a bound electron. As shown elsewhere,^{3,4,10,11} this expansion can be formally summed into a parametric integral:

$$\begin{aligned}
\bar{\mathbf{p}}(\bar{\mathbf{r}}, \bar{q}) = & -e \left[(\bar{q} - \bar{\mathbf{R}}) - \frac{1}{2!} (\bar{q} - \bar{\mathbf{R}})(\bar{q} - \bar{\mathbf{R}}) \cdot \bar{\nabla} + \dots \right] \delta(\bar{\mathbf{r}} - \bar{\mathbf{R}}) \\
= & -e (\bar{q} - \bar{\mathbf{R}}) \int_0^1 [1 - \lambda (\bar{q} - \bar{\mathbf{R}}) \cdot \bar{\nabla} + \dots] \delta(\bar{\mathbf{r}} - \bar{\mathbf{R}}) d\lambda \\
= & -e (\bar{q} - \bar{\mathbf{R}}) \int_0^1 \delta(\bar{\mathbf{r}} - \bar{\mathbf{R}} - \lambda (\bar{q} - \bar{\mathbf{R}})) d\lambda .
\end{aligned} \tag{2.19}$$

With this form of the electric polarization field, we show in the Appendix (see also Ref. 12) that

$$\frac{e}{c} \bar{\mathbf{a}}^{\perp}(\bar{q}) + \hbar \bar{\nabla}^{(q)} S(\bar{q}) = \frac{e}{c} \bar{\mathbf{a}}^{\perp}(\bar{q}) + \frac{1}{c} \bar{\nabla}^{(q)} \int \bar{\mathbf{p}}(\bar{\mathbf{r}}, \bar{q}) \cdot \bar{\mathbf{a}}^{\perp}(\bar{\mathbf{r}}) d^3 r = \int \bar{\mathbf{n}}(\bar{\mathbf{r}}, \bar{q}) \times \bar{\mathbf{b}}(\bar{\mathbf{r}}) d^3 r , \tag{2.20}$$

where

$$\begin{aligned}
\bar{\mathbf{n}}(\bar{\mathbf{r}}, \bar{q}) = & -e (\bar{q} - \bar{\mathbf{R}}) \int_0^1 \lambda \delta(\bar{\mathbf{r}} - \bar{\mathbf{R}} - \lambda (\bar{q} - \bar{\mathbf{R}})) d\lambda \\
= & -e \left[\frac{1}{2} (\bar{q} - \bar{\mathbf{R}}) - \frac{1}{3} (\bar{q} - \bar{\mathbf{R}})(\bar{q} - \bar{\mathbf{R}}) \cdot \bar{\nabla} + \dots \right] \delta(\bar{\mathbf{r}} - \bar{\mathbf{R}}) .
\end{aligned} \tag{2.21}$$

It is clear that using the first term of the expression for $\bar{\mathbf{n}}(\bar{\mathbf{r}}, \bar{q})$ in (2.20), we obtain the electric-quadrupole–magnetic-dipole result (2.17). With the use of the identity (2.20) in its full form, the multipolar Lagrangian for the general case becomes

$$\begin{aligned}
L_{\text{mult}} = & - \int \bar{\phi}(\bar{q}) \left[\frac{1}{2m} \left[-i\hbar \bar{\nabla}^{(q)} + \frac{1}{c} \int \bar{\mathbf{n}}(\bar{\mathbf{r}}, \bar{q}) \times \bar{\mathbf{b}}(\bar{\mathbf{r}}) d^3 r \right]^2 + V(\bar{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}(\bar{q}') \phi(\bar{q}')}{|\bar{q} - \bar{q}'|} d^3 q' \right] \phi(\bar{q}) d^3 q \\
& + \frac{i\hbar}{2} \int [\bar{\phi}(\bar{q}) \dot{\phi}(\bar{q}) - \dot{\bar{\phi}}(\bar{q}) \phi(\bar{q})] d^3 q - \frac{1}{c} \int \bar{\phi}(\bar{q}) \bar{\mathbf{p}}(\bar{\mathbf{r}}, \bar{q}) \cdot \dot{\bar{\mathbf{a}}}^{\perp}(\bar{\mathbf{r}}) \phi(\bar{q}) d^3 r d^3 q \\
& + \frac{1}{8\pi} \int \left[\left(\frac{\dot{\bar{\mathbf{a}}}^{\perp}(\bar{\mathbf{r}})}{c} \right)^2 - [\text{curl} \bar{\mathbf{a}}(\bar{\mathbf{r}})]^2 \right] d^3 r .
\end{aligned} \tag{2.22}$$

C. Equations of motion in multipolar form

It is instructive to derive the equations of motion in the first instance from the *electric dipole* Lagrangian (2.16). We have

$$\frac{\partial}{\partial t} \frac{\partial \mathcal{L}_{\text{mult}}}{\partial \dot{a}_i^{\perp}} = \frac{\ddot{a}_i^{\perp}(\bar{\mathbf{r}})}{4\pi c^2} + \frac{e}{c} \frac{d}{dt} \int \bar{\phi}(\bar{q}) (\bar{q} - \bar{\mathbf{R}})_j \delta_{ij}^{\perp}(\bar{\mathbf{r}} - \bar{\mathbf{R}}) \phi(\bar{q}) d^3 q , \tag{2.23}$$

$$\frac{\partial}{\partial t} \frac{\partial \mathcal{L}_{\text{mult}}}{\partial (\partial a_i^{\perp} / \partial x_j)} = - \frac{1}{4\pi} \frac{\partial}{\partial x_j} \left[\frac{\partial a_i^{\perp}(\bar{\mathbf{r}})}{\partial x_j} - \frac{\partial a_j^{\perp}(\bar{\mathbf{r}})}{\partial x_i} \right] , \tag{2.24}$$

$$\frac{\partial}{\partial a_i^{\perp}} \mathcal{L}_{\text{mult}} = 0 . \tag{2.25}$$

The Euler-Lagrange equation (2.4) becomes

$$\frac{\partial}{\partial t} \left[\frac{\dot{a}_i^{\perp}(\bar{\mathbf{r}})}{4\pi c} + \frac{e}{c} \int \bar{\phi}(\bar{q}) (\bar{q} - \bar{\mathbf{R}})_j \delta_{ij}^{\perp}(\bar{\mathbf{r}} - \bar{\mathbf{R}}) \phi(\bar{q}) d^3 q \right] + \frac{1}{4\pi} [\text{curl} \bar{\mathbf{b}}(\bar{\mathbf{r}})]_i = 0 , \tag{2.26}$$

that is,

$$\text{curl } \vec{b}(\vec{r}) = \frac{1}{c} \frac{\partial \vec{d}^{\perp}(\vec{r})}{\partial t}, \quad (2.27)$$

where $\vec{d}(\vec{r})$ is the displacement vector in the electric dipole approximation and is given by

$$\vec{d}(\vec{r}) = \vec{e}(\vec{r}) - 4\pi e \int \bar{\phi}(\vec{q})(\vec{q} - \vec{R})\delta(\vec{r} - \vec{R})\phi(\vec{q})d^3q. \quad (2.28)$$

The equation of motion for the electron field follows from

$$\frac{\partial}{\partial t} \frac{\partial \mathcal{L}_{\text{mult}}}{\partial \dot{\bar{\phi}}} = -\frac{i\hbar}{2} \dot{\phi}(\vec{q}), \quad (2.29)$$

$$\frac{\partial}{\partial x_j} \frac{\partial \mathcal{L}_{\text{mult}}}{\partial (\partial \bar{\phi} / \partial x_j)} = 0, \quad (2.30)$$

$$\frac{\partial \mathcal{L}_{\text{mult}}}{\partial \bar{\phi}} = - \left[-\frac{\hbar^2}{2m} (\nabla^{(q)})^2 + V(\vec{q}) + e^2 \int \frac{\bar{\phi}(\vec{q}')\phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \phi(\vec{q}) + \frac{i\hbar}{2} \dot{\phi}(\vec{q}) + \frac{e}{c} (\vec{q} - \vec{R}) \cdot \dot{\vec{a}}^{\perp}(\vec{R})\phi(\vec{q}). \quad (2.31)$$

Thus we obtain the familiar Schrödinger equation for a particle in a field in the electric dipole approximation:

$$i\hbar \dot{\phi}(\vec{q}) = \left[-\frac{\hbar^2}{2m} (\nabla^{(q)})^2 + V(\vec{q}) + e^2 \int \frac{\bar{\phi}(\vec{q}')\phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' + e(\vec{q} - \vec{R}) \cdot \vec{e}^{\perp}(\vec{R}) \right] \phi(\vec{q}). \quad (2.32)$$

The coupled equations (2.27) and (2.32) form the starting point for electrodynamics in this approximation.

Returning to the general case, we find from Lagrangian (2.22),

$$\frac{\partial}{\partial t} \frac{\partial \mathcal{L}_{\text{mult}}}{\partial \dot{a}_i} = \frac{\ddot{a}_i^{\perp}(\vec{r})}{4\pi c^2} - \frac{1}{c} \frac{d}{dt} \int \bar{\phi}(\vec{q}) p_i^{\perp}(\vec{r}, \vec{q}) \phi(\vec{q}) d^3q \quad (2.33)$$

and

$$\begin{aligned} \frac{\partial}{\partial x_j} \frac{\partial \mathcal{L}_{\text{mult}}}{\partial (\partial a_i / \partial x_j)} - \frac{\partial \mathcal{L}_{\text{mult}}}{\partial a_i} \\ = \frac{1}{4\pi} [\text{curl curl } \vec{a}(\vec{r})]_i \\ + \frac{1}{2mc} \epsilon_{ilm} \epsilon_{jkm} \int \bar{\phi}(\vec{q}) \left[\left[-i\hbar \nabla_j^{(q)} + \frac{1}{c} \int [\vec{n}(\vec{r}', \vec{q}) \times \vec{b}(\vec{r}')]_j d^3r' \right] \nabla_l n_k(\vec{r}, \vec{q}) \right. \\ \left. + \nabla_l n_k(\vec{r}, \vec{q}) \left[-i\hbar \nabla_j^{(q)} + \frac{1}{c} \int [\vec{n}(\vec{r}', \vec{q}) \times \vec{b}(\vec{r}')]_j d^3r' \right] \right] \phi(\vec{q}) d^3q. \end{aligned} \quad (2.34)$$

Thus the equation of motion for the electromagnetic field is

$$\frac{d}{dt} \left[-\frac{\dot{\vec{a}}^{\perp}(\vec{r})}{4\pi c^2} + \frac{1}{c} \int \bar{\phi}(\vec{q}) \vec{p}^{\perp}(\vec{r}, \vec{q}) \phi(\vec{q}) d^3q \right] = \frac{1}{4\pi} \text{curl} \left[\vec{b}(\vec{r}) - 4\pi \int \bar{\phi}(\vec{q}) \vec{m}(\vec{r}, \vec{q}) \phi(\vec{q}) d^3q \right], \quad (2.35)$$

where

$$\begin{aligned} \vec{m}(\vec{r}, \vec{q}) = \frac{1}{2mc} \left[\vec{n}(\vec{r}, \vec{q}) \times \left[-i\hbar \vec{\nabla}^{(q)} + \frac{1}{c} \int \vec{n}(\vec{r}', \vec{q}) \times \vec{b}(\vec{r}') d^3r' \right] \right] \\ - \frac{1}{2mc} \left[\left[-i\hbar \vec{\nabla}^{(q)} + \frac{1}{c} \int \vec{n}(\vec{r}', \vec{q}) \times \vec{b}(\vec{r}') d^3r' \right] \times \vec{n}(\vec{r}, \vec{q}) \right]. \end{aligned} \quad (2.36)$$

In terms of auxiliary fields $\vec{d}(\vec{r})$ and $\vec{h}(\vec{r})$ defined by

$$\vec{d}(\vec{r}) = \vec{e}(\vec{r}) + 4\pi \vec{p}(\vec{r}), \quad (2.37)$$

$$\vec{h}(\vec{r}) = \vec{b}(\vec{r}) - 4\pi \vec{m}(\vec{r}), \quad (2.38)$$

where

$$\vec{p}(\vec{r}) = \int \bar{\phi}(\vec{q}) \vec{p}(\vec{r}, \vec{q}) \phi(\vec{q}) d^3q, \quad (2.39)$$

$$\vec{m}(\vec{r}) = \int \bar{\phi}(\vec{q}) \vec{m}(\vec{r}, \vec{q}) \phi(\vec{q}) d^3q, \quad (2.40)$$

Eq. (2.53) becomes

$$\text{curl} \vec{h}(\vec{r}) = \frac{1}{c} \frac{\partial \vec{d}^\perp(\vec{r})}{\partial t}. \quad (2.41)$$

Equation (2.41) is the transverse part of the atomic field equation

$$\text{curl} \vec{H}(\vec{r}) = \frac{1}{c} \frac{\partial \vec{D}(\vec{r})}{\partial t} + \frac{4\pi}{c} \vec{J}^{\text{true}}(\vec{r}). \quad (2.42)$$

As we are dealing with neutral systems, there are no true charges and currents, so that $\vec{D}^\parallel(\vec{r})=0$ and $\vec{J}^{\text{true}}(\vec{r})=0$.

The equation of motion for the electron field $\phi(\vec{q})$ is found from

$$\frac{\partial}{\partial t} \frac{\partial \mathcal{L}_{\text{mult}}}{\partial \dot{\phi}} = \frac{-i\hbar}{2} \dot{\phi}(\vec{q}) \quad (2.43)$$

and

$$\begin{aligned} \frac{\partial}{\partial x_j} \frac{\partial \mathcal{L}_{\text{mult}}}{\partial (\partial \bar{\phi} / \partial x_j)} - \frac{\partial \mathcal{L}_{\text{mult}}}{\partial \bar{\phi}} = & \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{1}{c} \int \vec{n}(\vec{r}, \vec{q}) \times \vec{b}(\vec{r}) d^3r \right]^2 + V(\vec{q}) \right. \\ & \left. + e^2 \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \phi(\vec{q}) - \frac{i\hbar}{2} \dot{\phi}(\vec{q}) + \frac{1}{c} \int \vec{p}(\vec{r}, \vec{q}) \cdot \vec{a}^\perp(\vec{r}) d^3r \phi(\vec{q}) \end{aligned} \quad (2.44)$$

to be

$$i\hbar \dot{\phi}(\vec{q}) = \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{1}{c} \int \vec{n}(\vec{r}, \vec{q}) \times \vec{b}(\vec{r}) d^3r \right]^2 + V(\vec{q}) + e^2 \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' - \int \vec{p}(\vec{r}, \vec{q}) \cdot \vec{e}^\perp(\vec{r}) d^3r \right] \phi(\vec{q}). \quad (2.45)$$

Equation (2.45), which includes all multipole interactions, is the generalized version of (2.32).

To express the magnetic interactions in more familiar terms, we use expression (2.36) for the magnetization field, and rewrite (2.45) as

$$\begin{aligned} i\hbar \dot{\phi}(\vec{q}) = & \left[-\frac{\hbar^2}{2m} (\nabla^{(q)})^2 + V(\vec{q}) + e^2 \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' - \int \vec{p}(\vec{r}, \vec{q}) \cdot \vec{e}^\perp(\vec{r}) d^3r \right. \\ & \left. - \int \vec{m}(\vec{r}, \vec{q}) \cdot \vec{b}(\vec{r}) d^3r + \frac{1}{2mc^2} \left[\int \vec{n}(\vec{r}, \vec{q}) \times \vec{b}(\vec{r}) d^3r \right]^2 \right] \phi(\vec{q}). \end{aligned} \quad (2.46)$$

The leading terms of $\vec{m}(\vec{r}, \vec{q})$ and $\vec{n}(\vec{r}, \vec{q})$ are

$$\vec{m}(\vec{r}, \vec{q}) = -\frac{e}{2mc} (\vec{q} - \vec{R}) \times (-i\hbar \vec{\nabla}^{(q)}) \delta(\vec{r} - \vec{R}) \quad (2.47)$$

and

$$\vec{n}(\vec{r}, \vec{q}) = -\frac{e}{2} (\vec{q} - \vec{R}) \delta(\vec{r} - \vec{R}). \quad (2.48)$$

Thus in the magnetic dipole approximation, the linear magnetic interaction in (2.46) is the familiar

$$\frac{e}{2mc} [(\vec{q} - \vec{R}) \times (-i\hbar \vec{\nabla}^{(q)})] \cdot \vec{b}(\vec{R}) \quad (2.49)$$

and the quadratic magnetic interaction

$$\frac{e^2}{8mc^2} [(\vec{q} - \vec{R}) \times \vec{b}(\vec{R})]^2 \quad (2.50)$$

the well-known diamagnetic susceptibility energy.

We conclude this section by emphasizing that the coupled equations (2.41) and (2.46) that follow from the multipolar Lagrangian in its full form serve as the natural basis for the electrodynamics of the interaction of radiation with atoms and molecules.

III. CANONICAL FORMALISM AND HAMILTONIANS

Quantum electrodynamics based upon quantization of the Maxwell field and second quantization of the electron

field is most conveniently formulated in canonical terms. The standard procedure begins with the defining of the conjugate fields from the appropriate Lagrangian; these fields are then used to construct the Hamiltonian. The two forms of the Lagrangian discussed in Sec. II lead to the minimal-coupling and multipolar Hamiltonians. In this section we derive these two forms and discuss their relationship.

For the minimal-coupling case, the fields canonically conjugate to $\vec{a}^\perp(\vec{r})$, $\psi(\vec{q})$, and $\bar{\psi}(\vec{q})$ are

$$\pi_i(\vec{r}) = \frac{\partial \mathcal{L}_{\text{min}}}{\partial \dot{a}_i^\perp(\vec{r})} = \frac{\dot{a}_i^\perp(\vec{r})}{4\pi c^2} = -\frac{e_i^\perp(\vec{r})}{4\pi c}, \quad (3.1)$$

$$\Pi(\vec{q}) = \frac{\partial \mathcal{L}_{\text{min}}}{\partial \dot{\psi}(\vec{q})} = \frac{i\hbar}{2} \bar{\psi}(\vec{q}), \quad (3.2)$$

$$\bar{\Pi}(\vec{q}) = \frac{\partial \mathcal{L}_{\text{min}}}{\partial \dot{\bar{\psi}}(\vec{q})} = -\frac{i\hbar}{2} \psi(\vec{q}). \quad (3.3)$$

We note that the momentum conjugate to the vector potential is proportional to the transverse electric field. For the electron fields, the canonical conjugates are essentially the Hermitian conjugates of the fields themselves. This

property is a consequence of the fact that their equations of motion are first order in time. This feature, which is well known⁹ for the uncoupled electron fields, presents no difficulties in the development. The electron field depen-

dence in the Hamiltonian is best expressed in terms of ψ and $\bar{\psi}$ using (3.2) and (3.3). The minimal-coupling Hamiltonian is

$$\begin{aligned}
 H_{\min} &= \int \bar{\pi}(\vec{r}) \cdot \dot{\vec{a}}^{\perp}(\vec{r}) d^3r + \int \Pi(\vec{q}) \dot{\psi}(\vec{q}) d^3q + \int \bar{\Pi}(\vec{q}) \dot{\bar{\psi}}(\vec{q}) d^3q - L_{\min} \\
 &= \int \bar{\phi}(\vec{q}) \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{1}{c} \int \bar{\mathbf{n}}(\vec{r}, \vec{q}) \times \vec{\mathbf{b}}(\vec{r}) d^3r \right]^2 + V(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \phi(\vec{q}) d^3q \\
 &\quad + \frac{1}{8\pi} \int \{ [4\pi c \bar{\pi}(\vec{r})]^2 + [\text{curl} \vec{\mathbf{a}}(\vec{r})]^2 \} d^3r
 \end{aligned} \tag{3.4}$$

which may be partitioned in the usual way according to

$$H_{\min} = H_{\text{mol}}^{\min} + H_{\text{rad}}^{\min} + H_{\text{int}}^{\min}, \tag{3.5}$$

where

$$\begin{aligned}
 H_{\text{mol}}^{\min} &= \int \bar{\psi}(\vec{q}) \left[-\frac{\hbar^2}{2m} (\nabla^{(q)})^2 + V(\vec{q}) \right. \\
 &\quad \left. + \frac{e^2}{2} \int \frac{\bar{\psi}(\vec{q}') \psi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \psi(\vec{q}) d^3q, \\
 H_{\text{rad}}^{\min} &= \frac{1}{8\pi} \int \{ [4\pi c \bar{\pi}(\vec{r})]^2 + [\text{curl} \vec{\mathbf{a}}(\vec{r})]^2 \} d^3r \\
 &= \frac{1}{8\pi} \int [\bar{\mathbf{e}}^{\perp 2}(\vec{r}) + \vec{\mathbf{b}}^{\perp 2}(\vec{r})] d^3r,
 \end{aligned} \tag{3.6}$$

and

$$\begin{aligned}
 H_{\text{int}}^{\min} &= \frac{e}{mc} \int \bar{\psi}(\vec{q}) [-i\hbar \vec{\nabla}^{(q)} \cdot \vec{\mathbf{a}}^{\perp}(\vec{q})] \psi(\vec{q}) d^3q \\
 &\quad + \frac{e^2}{2mc^2} \int \bar{\psi}(\vec{q}) \vec{\mathbf{a}}^{\perp 2}(\vec{q}) \psi(\vec{q}) d^3q.
 \end{aligned} \tag{3.9}$$

We now turn our attention to the multipolar development. The analogs of (3.1)–(3.3) are

$$\begin{aligned}
 H_{\text{mult}} &= \int \bar{\pi}(\vec{r}) \cdot \dot{\vec{a}}^{\perp}(\vec{r}) d^3r + \int \Pi(\vec{q}) \dot{\phi}(\vec{q}) d^3q + \int \bar{\Pi}(\vec{q}) \dot{\bar{\phi}}(\vec{q}) d^3q - L_{\text{mult}} \\
 &= \int \bar{\phi}(\vec{q}) \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{1}{c} \int \bar{\mathbf{n}}(\vec{r}, \vec{q}) \times \vec{\mathbf{b}}(\vec{r}) d^3r \right]^2 + V(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \phi(\vec{q}) d^3q \\
 &\quad + \frac{1}{8\pi} \int \left[16\pi^2 \left[c \bar{\pi}(\vec{r}) + \int \bar{\phi}(\vec{q}) \vec{\mathbf{p}}^{\perp}(\vec{r}, \vec{q}) \phi(\vec{q}) d^3q \right]^2 + [\text{curl} \vec{\mathbf{a}}(\vec{r})]^2 \right] d^3r.
 \end{aligned} \tag{3.13}$$

We partition (3.13) into three terms: The first, H_{mol} , is independent of the electromagnetic field, the second, H_{rad} , is independent of the electron field, and the third, H_{int} , couples the two fields. Thus

$$H_{\text{mult}} = H_{\text{mol}}^{\text{mult}} + H_{\text{rad}}^{\text{mult}} + H_{\text{int}}^{\text{mult}}, \tag{3.14}$$

where

$$\begin{aligned}
 H_{\text{mol}}^{\text{mult}} &= \int \bar{\phi}(\vec{q}) \left[-\frac{\hbar^2}{2m} (\nabla^{(q)})^2 + V(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \phi(\vec{q}) d^3q + 2\pi \int \left[\int \bar{\phi}(\vec{q}) \vec{\mathbf{p}}^{\perp}(\vec{r}, \vec{q}) \phi(\vec{q}) d^3q \right]^2 d^3r, \\
 H_{\text{rad}}^{\text{mult}} &= \frac{1}{8\pi} \int [\bar{\mathbf{e}}^{\perp 2}(\vec{r}) + \vec{\mathbf{b}}^{\perp 2}(\vec{r})] d^3r, \\
 H_{\text{int}}^{\text{mult}} &= \frac{e}{mc} \int \bar{\psi}(\vec{q}) [-i\hbar \vec{\nabla}^{(q)} \cdot \vec{\mathbf{a}}^{\perp}(\vec{q})] \psi(\vec{q}) d^3q + \frac{e^2}{2mc^2} \int \bar{\psi}(\vec{q}) \vec{\mathbf{a}}^{\perp 2}(\vec{q}) \psi(\vec{q}) d^3q.
 \end{aligned} \tag{3.15}$$

$$\begin{aligned}
 \pi_i(\vec{r}) &= \frac{\partial \mathcal{L}_{\text{mult}}}{\partial \dot{a}_i^{\perp}} = \frac{\dot{a}_i^{\perp}(\vec{r})}{4\pi c^2} - \frac{1}{c} \int \bar{\phi}(\vec{q}) p_i^{\perp}(\vec{r}, \vec{q}) \phi(\vec{q}) d^3q \\
 &= -\frac{1}{4\pi c} \dot{a}_i^{\perp}(\vec{r}),
 \end{aligned} \tag{3.10}$$

$$\Pi(\vec{q}) = \frac{\partial \mathcal{L}_{\text{mult}}}{\partial \dot{\phi}} = \frac{i\hbar}{2} \bar{\phi}(\vec{q}), \tag{3.11}$$

and

$$\bar{\Pi}(\vec{q}) = \frac{\partial \mathcal{L}_{\text{mult}}}{\partial \dot{\bar{\phi}}} = -\frac{i\hbar}{2} \phi(\vec{q}). \tag{3.12}$$

The momentum conjugate to the vector potential is now proportional to the transverse component of the displacement vector field $\vec{\mathbf{d}}^{\perp}(\vec{r})$ of Eq. (2.37), in contrast to the minimal-coupling case where the conjugate momentum is proportional to the transverse component of the electric field. This distinction is already known^{7,13,14} in the treatments involving point particles interacting with radiation. The momenta conjugate to the electron fields are also different in the two cases; they are related through (2.9). For the conjugate momenta the same symbols are used in both cases, the context being sufficient to distinguish them. The Hamiltonian is now

$$H_{\text{rad}}^{\text{mult}} = \frac{1}{8\pi} \int \{ [4\pi c \vec{\pi}(\vec{r})]^2 + [\text{curl} \vec{a}(\vec{r})]^2 \} d^3r \quad (3.16)$$

$$= \frac{1}{8\pi} \int [\vec{d}^{\perp 2}(\vec{r}) + \vec{b}^2(\vec{r})] d^3r, \quad (3.17)$$

$$H_{\text{int}}^{\text{mult}} = - \int \vec{\phi}(\vec{q}) \vec{p}(\vec{r}, \vec{q}) \cdot \vec{d}^{\perp}(\vec{r}) \phi(\vec{q}) d^3r d^3q \\ - \int \vec{\phi}(\vec{q}) \vec{m}(\vec{r}, \vec{q}) \cdot \vec{b}(\vec{r}) \phi(\vec{q}) d^3r d^3q + \frac{1}{2mc^2} \int \vec{\phi}(\vec{q}) \left[\int \vec{n}(\vec{r}, \vec{q}) \times \vec{b}(\vec{r}) d^3r \right]^2 \phi(\vec{q}) d^3q. \quad (3.18)$$

An approximate $H_{\text{int}}^{\text{mult}}$ can be obtained by taking the first few terms in the multipolar expansions for the polarization fields. With the electric polarization current to the quadrupole order, and the magnetization correct to the dipole order, $H_{\text{int}}^{\text{mult}}$ takes the familiar form

$$H_{\text{int}}^{\text{mult}} \simeq - \int \vec{\phi}(\vec{q}) \vec{\mu} \cdot \vec{d}^{\perp}(\vec{R}) \phi(\vec{q}) d^3q - \int \vec{\phi}(\vec{q}) \vec{Q} \cdot \nabla \vec{d}^{\perp}(\vec{R}) \phi(\vec{q}) d^3q - \int \vec{\phi}(\vec{q}) \vec{m} \cdot \vec{b}(\vec{R}) \phi(\vec{q}) d^3q \\ + \frac{e^2}{8mc^2} \int \vec{\phi}(\vec{q}) [(\vec{q} - \vec{R}) \times \vec{b}(\vec{R})]^2 \phi(\vec{q}) d^3q. \quad (3.19)$$

Both Hamiltonians can be considered as the sum of electron and electromagnetic field energies, each of which consists of kinetic and potential energy contributions. For the electromagnetic field energy, we have

$$E_{\text{rad}} = \frac{1}{8\pi} \int \left[\left(\frac{\dot{\vec{a}}^{\perp}(\vec{r})}{4\pi c} \right)^2 + [\text{curl} \vec{a}(\vec{r})]^2 \right] d^3r \\ = \frac{1}{8\pi} \int (\vec{e}^{\perp 2} + \vec{b}^2) d^3r, \quad (3.20)$$

where the electric contribution is conventionally considered as the kinetic energy and the magnetic contribution as the potential energy. The difference between the minimal and multipolar forms depends on the relationship between $\dot{\vec{a}}^{\perp}(r)$ and the canonical momentum $\vec{\pi}(\vec{r})$. In the minimal coupling case, $\dot{\vec{a}}^{\perp}(r)$ is $4\pi c^2 \vec{\pi}(\vec{r})$, whereas for the multipolar case $\dot{\vec{a}}^{\perp}(r)$ is $4\pi c [c \vec{\pi}(\vec{r}) + \vec{p}^{\perp}(\vec{r})]$. For the electron field energy, we have

$$E_{\text{mol}} = \int \bar{\psi}(\vec{q}) \left[\frac{1}{2} m \dot{\vec{q}}^2 + V(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\psi}(\vec{q}') \psi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \psi(\vec{q}) d^3q \\ = \int \bar{\phi}(\vec{q}) \left[\frac{1}{2} m \dot{\vec{q}}^2 + V(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \phi(\vec{q}) d^3q, \quad (3.21)$$

where the kinetic energy contribution depends on $\dot{\vec{q}}$, the operator representative of which depends on the relationship between $\dot{\vec{q}}$ and the canonical momentum of the particle, already known in the particle–electromagnetic-field theory. For the minimal-coupling case, this relationship is

$$m \dot{\vec{q}} = \vec{p} + \frac{e}{c} \vec{a}^{\perp}(\vec{q}) \quad (3.22)$$

and for the multipolar case it is

$$m \dot{\vec{q}} = \vec{p} + \int \vec{n}(\vec{r}, \vec{q}) \times \vec{b}(\vec{r}) d^3r. \quad (3.23)$$

Thus we see that both Hamiltonians can be written in the form of (3.24)

$$H = (T + V)_{\text{electron}} + (T + V)_{\text{rad}}, \quad (3.24)$$

where the systems are apparently uncoupled. Despite this superficial partitioning, they are in fact coupled, and the interaction terms in the Hamiltonians can be explicitly recovered when the velocities are expressed in terms of the canonical momenta.

IV. QUANTUM CANONICAL TRANSFORMATION

The quantization of the dynamical system described by the Hamiltonians H_{min} and H_{mult} follows the well-known procedure of promoting the canonical variables to quantum operators. The canonically conjugate pairs obey the equal-time commutation (or anticommutation) relations

$$[a_i^{\perp}(\vec{r}), \pi_j(\vec{r}')]_{-} = i \hbar \delta_{ij}^{\perp}(\vec{r} - \vec{r}'), \quad (4.1)$$

$$[\psi(\vec{q}), \bar{\psi}(\vec{q}')]_{+} = [\phi(\vec{q}), \bar{\phi}(\vec{q}')]_{+} = \delta(\vec{q} - \vec{q}'). \quad (4.2)$$

All other pairs of operators commute (or anticommute). The minimal and multipolar Hamiltonians quantized in this way are related by a quantum canonical transformation which is a generalization of the classical coordinate transformation of the Lagrangian discussed in Sec. II. Under this canonical transformation, the conjugate pairs transform according to

$$\vec{a}_{\text{min}}^{\perp}(\vec{r}) = e^{-i\mathcal{S}} \vec{a}_{\text{mult}}^{\perp}(\vec{r}) e^{i\mathcal{S}}, \quad (4.3)$$

$$\vec{\pi}_{\text{min}}(\vec{r}) = e^{-i\mathcal{S}} \vec{\pi}_{\text{mult}}(\vec{r}) e^{i\mathcal{S}}, \quad (4.4)$$

$$\psi(\vec{q}) = e^{-i\mathcal{S}} \phi(\vec{q}) e^{i\mathcal{S}}, \quad (4.5)$$

$$\begin{aligned} \Pi_{\min}(\vec{q}) &= \frac{i\hbar}{2} \bar{\psi}(\vec{q}) = e^{-i\mathcal{S}} \frac{i\hbar}{2} \bar{\phi}(\vec{q}) e^{i\mathcal{S}} \\ &= e^{-i\mathcal{S}} \Pi_{\text{mult}}(\vec{q}) e^{i\mathcal{S}}. \end{aligned} \quad (4.6)$$

Clearly, the commutation and anticommutation relations (4.1) and (4.2) remain unaltered under this transformation. To obtain the transformed Hamiltonian we substitute (4.3)–(4.6) in H_{\min} . Thus

$$\begin{aligned} H_{\min}(\vec{a}_{\min}^{\perp}(\vec{r}), \vec{\pi}_{\min}(\vec{r}); \psi(\vec{q}), \bar{\psi}(\vec{q})) &= H_{\min}(e^{-i\mathcal{S}} \vec{a}_{\text{mult}}^{\perp}(\vec{r}) e^{i\mathcal{S}}, e^{-i\mathcal{S}} \vec{\pi}_{\text{mult}}(\vec{r}) e^{i\mathcal{S}}; e^{-i\mathcal{S}} \phi(\vec{q}) e^{i\mathcal{S}}, e^{-i\mathcal{S}} \bar{\phi}(\vec{q}) e^{i\mathcal{S}}) \\ &= e^{-i\mathcal{S}} H_{\min}(\vec{a}_{\text{mult}}^{\perp}(\vec{r}), \vec{\pi}_{\text{mult}}(\vec{r}); \phi(\vec{q}), \bar{\phi}(\vec{q})) e^{i\mathcal{S}}. \end{aligned} \quad (4.7)$$

The resultant expression is the multipolar Hamiltonian, i.e.,

$$H_{\text{mult}}(\vec{a}_{\text{mult}}^{\perp}(\vec{r}), \vec{\pi}_{\text{mult}}(\vec{r}); \phi(\vec{q}), \bar{\phi}(\vec{q})) = e^{-i\mathcal{S}} H_{\min}(\vec{a}_{\text{mult}}^{\perp}(\vec{r}), \vec{\pi}_{\text{mult}}(\vec{r}); \phi(\vec{q}), \bar{\phi}(\vec{q})) e^{i\mathcal{S}}. \quad (4.8)$$

Thus the transformation can also be viewed as a unitary rotation on the operator H_{\min} . This was the point of view adopted in our earlier work.^{2,7} The choice of the generator \mathcal{S} corresponding to the previous canonical transformation is, in terms of $S(\vec{q})$ defined by (2.10),

$$\mathcal{S} = \int \bar{\phi}(\vec{q}) S(\vec{q}) \phi(\vec{q}) d^3q = \frac{1}{\hbar c} \int \bar{\phi}(\vec{q}) \vec{p}(\vec{r}, \vec{q}) \cdot \vec{a}^{\perp}(\vec{r}) \phi(\vec{q}) d^3q d^3r \quad (4.9)$$

with $\vec{p}(\vec{r}, \vec{q})$ given by (2.19). For this \mathcal{S} , it is easily seen that the vector potential remains unaltered and we can therefore omit the suffix on $\vec{a}^{\perp}(\vec{r})$. However, the momentum conjugate to the vector potential does change. From (4.4) we have

$$\begin{aligned} \vec{\pi}_{\min}(\vec{r}) &= \vec{\pi}_{\text{mult}}(\vec{r}) - i[\mathcal{S}, \vec{\pi}_{\text{mult}}(\vec{r})]_{-} + \dots \\ &= \vec{\pi}_{\text{mult}}(\vec{r}) - \frac{i}{\hbar c} \int \bar{\phi}(\vec{q}) p_i(\vec{r}, \vec{q}) \phi(\vec{q}) d^3q [a_i^{\perp}(\vec{r}'), \vec{\pi}(\vec{r})]_{-} d^3r' \end{aligned} \quad (4.10)$$

$$= \vec{\pi}_{\text{mult}}(\vec{r}) + \frac{1}{c} \vec{p}^{\perp}(\vec{r}), \quad (4.11)$$

where $\vec{p}(\vec{r})$ is the polarization field. The series (4.10) terminates at the second term. We emphasize that although $\vec{\pi}_{\min}$ is proportional to the transverse electric field, the presence of $\vec{p}^{\perp}(\vec{r})$ in (4.11) results in $\vec{\pi}_{\text{mult}}$ being proportional to the transverse displacement field.

For the operator electron field, we have from (4.5)

$$\begin{aligned} \psi(\vec{q}) &= \phi(\vec{q}) - i[\mathcal{S}, \phi(\vec{q})]_{-} - \frac{1}{2!} [[\mathcal{S}, [\mathcal{S}, \phi(\vec{q})]_{-}]_{-} + \dots \\ &= \phi(\vec{q}) - i \int [\bar{\phi}(\vec{q}') S(\vec{q}') \phi(\vec{q}'), \phi(\vec{q})]_{-} d^3q' \\ &\quad - \frac{1}{2} \int [\bar{\phi}(\vec{q}') S(\vec{q}') \phi(\vec{q}'), [\bar{\phi}(\vec{q}'') S(\vec{q}'') \phi(\vec{q}''), \phi(\vec{q})]_{-}]_{-} d^3q' d^3q'' - \dots \end{aligned} \quad (4.12)$$

$$\begin{aligned} &= \phi(\vec{q}) + i \int S(\vec{q}') \phi(\vec{q}) \delta(\vec{q} - \vec{q}') d^3q' \\ &\quad - \frac{1}{2} \int S(\vec{q}') S(\vec{q}'') \delta(\vec{q} - \vec{q}') \delta(\vec{q} - \vec{q}'') \phi(\vec{q}) d^3q' d^3q'' - \dots = e^{iS(\vec{q})} \phi(\vec{q}). \end{aligned} \quad (4.13)$$

In contrast to (4.10), all terms in the series (4.12) contribute to (4.13). Similarly, Eq. (4.6) leads to the Hermitian conjugate equation $\bar{\psi}(\vec{q}) = \bar{\phi}(\vec{q}) e^{-iS(\vec{q})}$. We note that the second-quantized operator transformation (4.5) leading to (4.13) is the quantum analog of (2.9) for the first-quantized fields. The fact that the electron fields change in this way under the transformation requires concomitant changes in the equations of motion. In the minimal-coupling case, we have

$$\begin{aligned} i\hbar \dot{\psi}(\vec{q}) &= [\psi(\vec{q}), H_{\min}]_{-} \\ &= \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{e}{c} \vec{a}^{\perp}(\vec{q}) \right]^2 + V(\vec{q}) + e^2 \int \frac{\bar{\psi}(\vec{q}') \psi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \psi(\vec{q}). \end{aligned} \quad (4.14)$$

On the other hand, for the multipolar coupling case,

$$\begin{aligned} i\hbar \dot{\phi}(\vec{q}) &= [\phi(\vec{q}), H_{\text{mult}}]_{-} \\ &= \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{1}{c} \int \vec{n}(\vec{r}, \vec{q}) \times \vec{b}(\vec{r}) d^3r \right]^2 + V(\vec{q}) + e^2 \int \frac{\bar{\phi}(\vec{q}') \phi(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' + 4\pi c \int \vec{p}(\vec{r}, \vec{q}) \cdot \vec{\pi}_{\text{mult}}(\vec{r}) d^3r \right. \\ &\quad \left. + 4\pi \int \bar{\phi}(\vec{q}') \vec{p}^{\perp}(\vec{r}, \vec{q}') \phi(\vec{q}') d^3q' \cdot \vec{p}^{\perp}(\vec{r}, \vec{q}) d^3r \right] \phi(\vec{q}) \end{aligned} \quad (4.15)$$

which, with the use of the relationship connecting the electric field $\vec{e}^{\perp}(\vec{r})$ and the field $\vec{\pi}(\vec{r})$, conjugate to $\vec{a}^{\perp}(\vec{r})$, gives

$$i\hbar\dot{\phi}(\vec{q}) = \left[\frac{1}{2m} \left[-i\hbar\vec{\nabla}^{(q)} + \frac{1}{c} \int \vec{n}(\vec{r}, \vec{q}) \times \vec{b}(\vec{r}) d^3r \right]^2 + V(\vec{q}) + e^2 \int \frac{\vec{\phi}(\vec{q}')\phi(\vec{q}')}{|\vec{q}-\vec{q}'|} d^3q' - \int \vec{p}(\vec{r}, \vec{q}) \cdot \vec{e}^{\perp}(\vec{r}) d^3r \right] \phi(\vec{q}). \quad (4.16)$$

The operator equations (4.14) and (4.16) are the second-quantized equivalents of the first-quantized equations (2.8) and (2.45), respectively. That the two Schrödinger-type equations are different in form is not surprising since they are equations of motion for different fields.¹⁵ An alternative route to (4.16) is to begin with the equation of motion for $\psi(q)$ and to use the transformation (4.13). We have

$$\begin{aligned} i\hbar \frac{\partial \phi(\vec{q})}{\partial t} &= i\hbar \frac{\partial}{\partial t} [e^{-iS(\vec{q})} \psi(\vec{q})] = e^{-iS(\vec{q})} i\hbar \frac{\partial \psi}{\partial t} + \hbar \dot{S} \phi(\vec{q}) \\ &= e^{-iS(\vec{q})} \left[\frac{1}{2m} \left[-i\hbar\vec{\nabla}^{(q)} + \frac{e}{c} \vec{a}^{\perp}(\vec{q}) \right]^2 + V(\vec{q}) + e^2 \int \frac{\vec{\phi}(\vec{q}')\phi(\vec{q}')}{|\vec{q}-\vec{q}'|} d^3q' \right] e^{-iS(\vec{q})} \phi(\vec{q}) \\ &\quad + \frac{1}{c} \int \vec{p}(\vec{r}, \vec{q}) \cdot \dot{\vec{a}}^{\perp}(\vec{r}) d^3r \phi(\vec{q}) \end{aligned} \quad (4.17)$$

$$\begin{aligned} &= \left[\frac{1}{2m} \left[-i\hbar\vec{\nabla}^{(q)} + \frac{e}{c} \vec{a}^{\perp}(\vec{q}) + \vec{\nabla}^{(q)} \int \vec{p}(\vec{r}, \vec{q}) \cdot \vec{a}^{\perp}(\vec{r}) d^3r \right]^2 \right. \\ &\quad \left. + V(\vec{q}) + e^2 \int \frac{\vec{\phi}(\vec{q}')\phi(\vec{q}')}{|\vec{q}-\vec{q}'|} d^3q' - \int \vec{p}(\vec{r}, \vec{q}) \cdot \vec{e}^{\perp}(\vec{r}) d^3r \right] \phi(\vec{q}). \end{aligned} \quad (4.18)$$

With the aid of the identity (2.20), this equation is seen to be the same as (4.16), the equation in multipolar form.

V. EXTENSION TO A MOLECULAR ASSEMBLY

In the application of radiation theory to the study of intermolecular interactions, the multipolar formalism has distinct advantages over the minimal-coupling method. In this section, we extend the one-center theory developed in the earlier sections to a molecular assembly and draw attention to some of the salient features. To make this extension, it is convenient to introduce several electron fields, one associated with each molecule, and to assume kinematic independence of these fields. For molecules with weakly coupled chromophores, it is better to assume that the electron fields of the different chromophores are distinct. In the many-body theory, this corresponds to the imposition of the Pauli principle for the electrons associated with each molecule or chromophore and to the neglect of electron exchange between different centers. Let the electron wave field associated with center a be denoted by $\phi_a(\vec{q})$. Then the multipolar Lagrangian for the complete system, obtained by generalizing (2.22) and ignoring nuclear kinetic energy contributions, is

$$\begin{aligned} L_{\text{mult}} &= - \sum_a \int \bar{\phi}_a(\vec{q}) \left[\frac{1}{2m} \left[-i\hbar\vec{\nabla}^{(q)} + \frac{1}{c} \int \vec{n}_a(\vec{r}, \vec{q}) \times \vec{b}(\vec{r}) d^3r \right]^2 \right. \\ &\quad \left. + V_a(q) + \frac{e^2}{2} \int \frac{\bar{\phi}_a(\vec{q}')\phi_a(\vec{q}')}{|\vec{q}-\vec{q}'|} d^3q' \right] \phi_a(\vec{q}) d^3q \\ &\quad - \sum_{\substack{a,b \\ (a \neq b)}} \bar{\phi}_a(\vec{q}) \left[\frac{-Z_b e^2}{|\vec{q}-\vec{R}_b|} + \frac{e^2}{2} \int \frac{\bar{\phi}_b(\vec{q}')\phi_b(\vec{q}')}{|\vec{q}-\vec{q}'|} d^3q' \right] \phi_a(\vec{q}) d^3q \\ &\quad + \frac{1}{2} \sum_{\substack{a,b \\ (a \neq b)}} \frac{Z_a Z_b e^2}{|\vec{R}_a - \vec{R}_b|} + \frac{i\hbar}{2} \sum_a \int [\bar{\phi}_a(\vec{q})\dot{\phi}_a(\vec{q}) - \dot{\bar{\phi}}_a(\vec{q})\phi_a(\vec{q})] d^3q \\ &\quad - \frac{1}{c} \sum_a \int \bar{\phi}_a(\vec{q}) \vec{p}_a(\vec{r}, \vec{q}) \cdot \dot{\vec{a}}^{\perp}(\vec{r}) \phi_a(\vec{q}) d^2q d^3r + \frac{1}{8\pi} \int \left[\left[\frac{\dot{\vec{a}}^{\perp}(\vec{r})}{c} \right]^2 - [\text{curl} \vec{a}(\vec{r})]^2 \right] d^3r. \end{aligned} \quad (5.1)$$

In (5.1) it is assumed that the total nuclear charge for assembly a is $Z_a e$ and \vec{R}_a is a conveniently chosen center. $V(\vec{q})$ is the Coulombic potential energy between the nuclei of assembly a and between the electron field ϕ_a and these nuclei. The second and third terms of (5.1) are the intermolecular Coulombic contributions. Both the intra- and

inter-Coulombic terms can be expressed in terms of the longitudinal components of the total polarization field. We first note that these Coulombic terms are

$$\frac{1}{8\pi} \int |\vec{e}^{\parallel}(\vec{r})|^2 d^3r, \quad (5.2)$$

where $\bar{\epsilon}^{\parallel}(\vec{r})$ is the electrostatic field of all the charges. With the assumption that there are no net free charges,¹⁶ i.e., no ions or charged chromophores, $\text{div} \bar{\epsilon}^{\parallel}(\vec{r}) = -4\pi \text{div} \bar{p}^{\parallel}(\vec{r})$, and the Coulomb terms (5.2) are given by

$$2\pi \int |\bar{p}^{\parallel}(\vec{r})|^2 d^3r, \quad (5.3)$$

where

$$\begin{aligned} \bar{p}^{\parallel}(\vec{r}) &= \sum_a \bar{p}_a^{\parallel}(\vec{r}) \\ &= \sum_a \int \bar{\phi}_a(\vec{q}) \bar{p}_a^{\parallel}(\vec{r}, \vec{q}) \phi_a(\vec{q}) d^3q \end{aligned} \quad (5.4)$$

with $p_{ai}^{\parallel}(\vec{r}, \vec{q})$ given by

$$p_{ai}^{\parallel}(\vec{r}, \vec{q}) = \frac{e}{4\pi} \nabla_i \left[\frac{1}{|\vec{r} - \vec{q}|} - \frac{1}{|\vec{r} - \vec{R}_a|} \right] \quad (5.5)$$

$$= -e(\vec{q} - \vec{R}_a)_j \int_0^1 \delta_{ij}^{\parallel}(\vec{r} - \vec{R}_a - \lambda(\vec{q} - \vec{R}_a)) d\lambda \quad (5.6)$$

which is the longitudinal component of (2.19). Substituting (5.4) and (5.5) in (5.3) together with the normalization (5.7),

$$\int \bar{\phi}_a(\vec{q}) \phi_a(\vec{q}) d^3q = Z_a \quad (5.7)$$

a consequence of neutrality, we obtain the intra- and inter-Coulombic terms of (5.1):

$$\begin{aligned} V_{\text{intra}} &= 2\pi \sum_a \int \bar{p}_a^{\parallel}(\vec{r}) \cdot \bar{p}_a^{\parallel}(\vec{r}) d^3r \\ &= \sum_a \int \bar{\phi}_a(\vec{q}) \left[V_a(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}_a(\vec{q}') \phi_a(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \phi_a(\vec{q}) d^3q \end{aligned} \quad (5.8)$$

and

$$\begin{aligned} V_{\text{inter}} &= 2\pi \sum_{\substack{a,b \\ (a \neq b)}} \int \bar{p}_a^{\parallel}(\vec{r}) \cdot \bar{p}_b^{\parallel}(\vec{r}) d^3r \\ &= \sum_{\substack{a,b \\ (a \neq b)}} \int \bar{\phi}_a(\vec{q}) \left[\frac{-Z_b e^2}{|\vec{q} - \vec{R}_b|} + \frac{e^2}{2} \int \frac{\bar{\phi}_b(\vec{q}') \phi_b(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \phi_a(\vec{q}) d^3q + \frac{1}{2} \sum_{\substack{a,b \\ (a \neq b)}} \frac{Z_a Z_b e^2}{|\vec{R}_a - \vec{R}_b|}. \end{aligned} \quad (5.9)$$

Using (5.8) and (5.9) and completing the square in the last two terms of (5.1), we obtain the expression (5.10) for the multipolar Lagrangian. Thus

$$\begin{aligned} L_{\text{mult}} &= -\sum_a \int \bar{\phi}_a(\vec{q}) \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{1}{c} \int \bar{n}_a(\vec{r}, \vec{q}) \times \vec{b}(\vec{r}) d^3r \right]^2 \right] \phi_a(\vec{q}) d^3q \\ &\quad - V_{\text{intra}} - 2\pi \sum_{\substack{a,b \\ (a \neq b)}} \bar{p}_a^{\parallel}(\vec{r}) \cdot \bar{p}_b^{\parallel}(\vec{r}) d^3r - \frac{i\hbar}{2} \sum_a \int [\bar{\phi}_a(\vec{q}) \dot{\phi}_a(\vec{q}) - \dot{\bar{\phi}}_a(\vec{q}) \phi_a(\vec{q})] d^3q \\ &\quad + \frac{1}{8\pi} \int \left[\left[\frac{\dot{\bar{a}}^{\perp}(\vec{r})}{c} - 4\pi \bar{p}^{\perp}(\vec{r}) \right]^2 - [\text{curl} \bar{a}(\vec{r})]^2 \right] d^3r - 2\pi \int |\bar{p}^{\perp}(\vec{r})|^2 d^3r. \end{aligned} \quad (5.10)$$

As for the longitudinal term (5.3), we can also partition $2\pi \int |\bar{p}^{\perp}(\vec{r})|^2 d^3r$ into intra- and intermolecular contributions. The intermolecular parts of both integrals are then combined according to^{7,8}

$$2\pi \int |\bar{p}^{\perp}(\vec{r})|^2 d^3r + 2\pi \sum_{\substack{a,b \\ (a \neq b)}} \int \bar{p}_a^{\parallel}(\vec{r}) \cdot \bar{p}_b^{\parallel}(\vec{r}) d^3r = 2\pi \sum_a \int |\bar{p}_a^{\perp}(\vec{r})|^2 d^3r + 2\pi \sum_{\substack{a,b \\ (a \neq b)}} \int \bar{p}_a(\vec{r}) \cdot \bar{p}_b(\vec{r}) d^3r. \quad (5.11)$$

The fields $\bar{p}_a(\vec{r})$ in the last term of (5.11) are the total polarization fields and are localized at their respective centers. Thus for nonoverlapping systems this intermolecular term is zero. The field-independent one-center contribution of (5.11) can be added to the other one-center term of (5.8) to give an effective intramolecular potential energy

$$\begin{aligned} \bar{V}_a &= 2\pi \int |\bar{p}_a^{\perp}(\vec{r})|^2 d^3r \\ &\quad + \int \bar{\phi}_a(\vec{q}) \left[V_a(\vec{q}) + \frac{e^2}{2} \int \frac{\bar{\phi}_a(\vec{q}') \phi_a(\vec{q}')}{|\vec{q} - \vec{q}'|} d^3q' \right] \phi_a(\vec{q}) d^3q. \end{aligned} \quad (5.12)$$

Thus the multipolar Lagrangian can be written as

$$L_{\text{mult}} = - \sum_a \left\{ \int \bar{\phi}_a(\bar{q}) \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{1}{c} \int \bar{n}_a(\bar{r}, \bar{q}) \times \bar{b}(\bar{r}) d^3r \right]^2 \right] \phi_a(\bar{q}) d^3q + \bar{V}_a \right\} \\ + \frac{i\hbar}{2} \sum_a \int [\bar{\phi}_a(\bar{q}) \dot{\phi}_a(\bar{q}) - \dot{\bar{\phi}}_a(\bar{q}) \phi_a(\bar{q})] d^3q + \frac{1}{8\pi} \int \left[\left[\frac{\dot{\bar{a}}^\perp(\bar{r})}{c} - 4\pi \bar{p}^\perp(\bar{r}) \right]^2 - [\text{curl} \bar{a}(\bar{r})]^2 \right] d^3r. \quad (5.13)$$

An important feature of this Lagrangian is that there are no explicit contributions depending on pairs of molecules. All intermolecular interactions are mediated by the transverse electromagnetic field. This is in contrast to the minimal-coupling case where the electrostatic interaction terms between molecules explicitly appear in the Lagrangian and need to be considered in addition to the electromagnetic couplings.

The Hamiltonian is obtained in a straightforward manner following essentially the same lines as those described in Sec. III; the many-center analog of (3.14) is

$$H_{\text{mult}} = \sum_a H_{\text{mol}}^{\text{mult}}(a) + H_{\text{rad}}^{\text{mult}} + \sum_a H_{\text{int}}^{\text{mult}}(a). \quad (5.14)$$

In the minimal-coupling case, the Hamiltonian as well as the Lagrangian cannot be expressed in this simple additive form. H_{min} has interactions which are nonlocal involving pairs of molecules. The many-center analog of (3.5) is

$$H_{\text{min}} = \sum_a H_{\text{mol}}^{\text{min}}(a) + H_{\text{rad}}^{\text{min}} + \sum_a H_{\text{int}}^{\text{min}}(a) + \sum_{\substack{a,b \\ (a \neq b)}} V_{\text{inter}}(a,b), \quad (5.15)$$

where V_{inter} is given by the expression (5.9) with the ϕ 's replaced by the corresponding ψ 's. In the electric dipole approximation, the interaction terms of (5.15) become

$$H_{\text{int}}^{\text{min}}(a) = \frac{e}{mc} \int \bar{\psi}_a(\bar{q}) [-i\hbar \vec{\nabla}^{(q)} \cdot \bar{a}^\perp(\bar{R}_a)] \psi_a(\bar{q}) d^3q + \frac{Z_a e^2}{2mc^2} \bar{a}^{\perp 2}(\bar{R}_a), \quad (5.16)$$

$$V_{\text{inter}}(a,b) = \frac{e^2(\delta_{ij} - 3\hat{R}_i\hat{R}_j)}{R^3} \int \bar{\psi}_a(\bar{q}) \bar{\psi}_b(\bar{q}') (\bar{q} - \bar{R}_a)_i (\bar{q}' - \bar{R}_b)_j \psi_a(\bar{q}) \psi_b(\bar{q}') d^3q d^3q', \quad (5.17)$$

where $\bar{R} = \bar{R}_b - \bar{R}_a$. In contrast, the corresponding interaction energy in the multipolar Hamiltonian (5.14) takes the simpler form,

$$H_{\text{int}}^{\text{mult}}(a) = e \int \bar{\phi}_a(\bar{q}) (\bar{q} - \bar{R}_a) \cdot \bar{d}^\perp(\bar{R}_a) \phi_a(\bar{q}) d^3q. \quad (5.18)$$

Applications illustrating the use of the two formalisms with their differing interaction terms are given in papers II and III.

VI. DISCUSSION

In this paper we have made the transformation from the minimal-coupling formalism to the multipolar formalism by changing the generalized coordinates describing the electron fields. This contrasts with the procedure used in the particle-radiation-field theory where a total time derivative is added to the minimal-coupling Lagrangian, the generalized coordinates \bar{q} and \bar{a}^\perp remaining unchanged. In the latter case, the equation of motion for the particle is the Lorentz force law which is invariant to the transformation. However with the electron field as coordinates, the equations of motion are different because the fields themselves have changed under the transformation. In the electric dipole approximation, these Schrödinger-type equations are

$$i\hbar \dot{\psi}(\bar{q}) = \left[\frac{1}{2m} \left[-i\hbar \vec{\nabla}^{(q)} + \frac{e}{c} \bar{a}^\perp(\bar{R}) \right]^2 + V(\bar{q}) \right] \psi(\bar{q}) \quad (6.1)$$

and

$$i\hbar \dot{\phi}(\bar{q}) = \left[\frac{1}{2m} (-i\hbar \vec{\nabla}^{(q)})^2 + e(\bar{q} - \bar{R}) \cdot \bar{e}^\perp(\bar{R}) + V(\bar{q}) \right] \phi(\bar{q}), \quad (6.2)$$

where self-interactions have been omitted. As in the particle-radiation-field theory, the field canonically conjugate to the vector potential changes under the transformation:

$$\bar{\pi}_{\text{min}}(\bar{r}) = - \frac{\bar{e}^\perp(\bar{r})}{4\pi c}, \quad (6.3)$$

$$\bar{\pi}_{\text{mult}}(\bar{r}) = - \frac{\bar{e}^\perp(\bar{r})}{4\pi c} - \bar{p}^\perp(\bar{r}) \\ = - \frac{\bar{d}^\perp(\bar{r})}{4\pi c}. \quad (6.4)$$

Thus in the development of the Hamiltonian formalism, it is essential to recognize the changes in both the generalized coordinates and their conjugate fields. A consequence of this is that, within the canonical formalism, the electron field appearing in the equation of motion (6.2) must be expressed in terms of the displacement vector using (6.4). The equations of motion for the electromagnetic field are the Maxwell equations. When expressed in terms of the canonical variables appropriate to the two theories, they take different forms as given by Eqs. (2.6) and (2.41).

A significant feature of the multipolar formalism arising from the changes in the canonical variables is, as developed in Sec. V, that the electrostatic interactions between neutral molecules are not explicitly present in the Hamiltonian. All intermolecular interactions are mediated through the transverse radiation field.

APPENDIX: DERIVATION OF IDENTITY (2.20)

We begin by showing that $e^{-1} \int \bar{\mathbf{n}}(\bar{\mathbf{r}}', \bar{\mathbf{r}}) \times \bar{\mathbf{b}}(\bar{\mathbf{r}}') d^3 r'$ is a vector potential for the magnetic field $\bar{\mathbf{b}}(\bar{\mathbf{r}})$:

$$\begin{aligned} \text{curl} \left[e^{-1} \int \bar{\mathbf{n}}(\bar{\mathbf{r}}', \bar{\mathbf{r}}) \times \bar{\mathbf{b}}(\bar{\mathbf{r}}') d^3 r' \right] &= e^{-1} \int \bar{\nabla} \times [\bar{\mathbf{n}}(\bar{\mathbf{r}}', \bar{\mathbf{r}}) \times \bar{\mathbf{b}}(\bar{\mathbf{r}}')] d^3 r' \\ &= -e^{-1} \int \bar{\mathbf{b}}(\bar{\mathbf{r}}') \text{div} \bar{\mathbf{n}}(\bar{\mathbf{r}}', \bar{\mathbf{r}}) d^3 r' + e^{-1} \int [\bar{\mathbf{b}}(\bar{\mathbf{r}}') \cdot \bar{\nabla}] \bar{\mathbf{n}}(\bar{\mathbf{r}}', \bar{\mathbf{r}}) d^3 r' \end{aligned} \quad (\text{A1})$$

using (2.21) for $\bar{\mathbf{n}}(\bar{\mathbf{r}}', \bar{\mathbf{r}})$, the i th component of (A1), is

$$\begin{aligned} & \int b_i(\bar{\mathbf{r}}') \left[\text{div} \left[(\bar{\mathbf{r}} - \bar{\mathbf{R}}) \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda \right] d^3 r' \right] - \int [b_j(\bar{\mathbf{r}}') \nabla_j] (\bar{\mathbf{r}} - \bar{\mathbf{R}})_i \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' \\ &= 3 \int b_i(\bar{\mathbf{r}}') \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' - \int b_i(\bar{\mathbf{r}}') (\bar{\mathbf{r}} - \bar{\mathbf{R}})_j \int_0^1 \lambda^2 \nabla'_j \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' \\ &\quad - \int b_j(\bar{\mathbf{r}}') \delta_{ij} \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' + \int b_j(\bar{\mathbf{r}}') (\bar{\mathbf{r}} - \bar{\mathbf{R}})_i \int_0^1 \lambda^2 \nabla'_j \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' \\ &= 2 \int b_i(\bar{\mathbf{r}}') \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' + \int b_i(\bar{\mathbf{r}}') \int_0^1 \lambda^2 \frac{d}{d\lambda} \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' \\ &= \int b_i(\bar{\mathbf{r}}') \int_0^1 \frac{d}{d\lambda} [\lambda^2 \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}}))] d\lambda d^3 r' = b_i(\bar{\mathbf{r}}). \end{aligned} \quad (\text{A2})$$

We note, however, that this vector potential, in contrast to $\bar{\mathbf{a}}^\perp(\bar{\mathbf{r}})$, is not entirely transverse. The difference between the two potentials is the gradient of a scalar field. We have

$$\begin{aligned} & e^{-1} \int [\bar{\mathbf{n}}(\bar{\mathbf{r}}, \bar{\mathbf{r}}') \times \bar{\mathbf{b}}(\bar{\mathbf{r}}')]_i d^3 r' - a_i^\perp(\bar{\mathbf{r}}) \\ &= -\epsilon_{ijk} \epsilon_{lmk} \int (\bar{\mathbf{r}} - \bar{\mathbf{R}})_j [\nabla'_l a_m^\perp(\bar{\mathbf{r}}')] \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' - a_i^\perp(\bar{\mathbf{r}}) \\ &= -\int (\bar{\mathbf{r}} - \bar{\mathbf{R}})_j [\nabla'_j a_i^\perp(\bar{\mathbf{r}}')] \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' \\ &\quad + \int (\bar{\mathbf{r}} - \bar{\mathbf{R}})_j [\nabla'_j a_i^\perp(\bar{\mathbf{r}}')] \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' - a_i^\perp(\bar{\mathbf{r}}) \\ &= \int (\bar{\mathbf{r}} - \bar{\mathbf{R}})_j a_j^\perp(\bar{\mathbf{r}}') \nabla'_i \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' \\ &\quad - \int (\bar{\mathbf{r}} - \bar{\mathbf{R}})_j a_i^\perp(\bar{\mathbf{r}}') \nabla'_j \int_0^1 \lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' - a_i^\perp(\bar{\mathbf{r}}) \\ &= -\int (\bar{\mathbf{r}} - \bar{\mathbf{R}})_j a_j^\perp(\bar{\mathbf{r}}') \nabla'_i \int_0^1 \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' \\ &\quad + \int a_i^\perp(\bar{\mathbf{r}}') \int_0^1 \lambda \frac{d}{d\lambda} \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' - a_i^\perp(\bar{\mathbf{r}}) \\ &= -\nabla_i \int (\bar{\mathbf{r}} - \bar{\mathbf{R}})_j a_j^\perp(\bar{\mathbf{r}}') \int_0^1 \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' \\ &\quad + \int a_i^\perp(\bar{\mathbf{r}}') \int_0^1 \left[1 + \lambda \frac{d}{d\lambda} \right] \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' - a_i^\perp(\bar{\mathbf{r}}) \\ &= e^{-1} \nabla_i \left[-e(\bar{\mathbf{r}} - \bar{\mathbf{R}})_j \int a_j^\perp(\bar{\mathbf{r}}') \int_0^1 \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}})) d\lambda d^3 r' \right] \\ &\quad + \int a_i^\perp(\bar{\mathbf{r}}') \int_0^1 \frac{d}{d\lambda} [\lambda \delta(\bar{\mathbf{r}}' - \bar{\mathbf{R}} - \lambda(\bar{\mathbf{r}} - \bar{\mathbf{R}}))] d\lambda d^3 r' - a_i^\perp(\bar{\mathbf{r}}) \\ &= e^{-1} \nabla_i \int \bar{\mathbf{p}}(\bar{\mathbf{r}}', \bar{\mathbf{r}}) \cdot \bar{\mathbf{a}}^\perp(\bar{\mathbf{r}}') d^3 r', \end{aligned} \quad (\text{A3})$$

where we have used (2.19) for the polarization field $\bar{\mathbf{p}}(\bar{\mathbf{r}}', \bar{\mathbf{r}})$. Thus the scalar field whose gradient is the difference between two vector potentials is

$$e^{-1} \int \bar{\mathbf{p}}(\bar{\mathbf{r}}', \bar{\mathbf{r}}) \cdot \bar{\mathbf{a}}^\perp(\bar{\mathbf{r}}') d^3 r'.$$

For $\bar{\mathbf{r}} = \bar{\mathbf{q}}$, Eq. (A3) leads to the required identity

$$\frac{e}{c} \bar{\mathbf{a}}^\perp(\bar{\mathbf{q}}) + \frac{1}{c} \bar{\nabla}^{(q)} \int \bar{\mathbf{p}}(\bar{\mathbf{r}}', \bar{\mathbf{q}}) \cdot \bar{\mathbf{a}}^\perp(\bar{\mathbf{r}}') d^3 r' = \int \bar{\mathbf{n}}(\bar{\mathbf{r}}', \bar{\mathbf{q}}) \times \bar{\mathbf{b}}(\bar{\mathbf{r}}') d^3 r'. \quad (\text{A4})$$

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- ¹⁵K. Haller [*Phys. Rev. A* **26**, 1796 (1982)] raises, as a difficulty, the fact that these equations are distinct. The development given here shows that such a difference is a natural one.
- ¹⁶For systems carrying net charges, the argument needs more care due to the incomplete cancellation of the inter-Coulomb terms. This has been considered by E. A. Power and T. Thirunamachandran, *Proc. R. Soc. London Ser. A* **372**, 265 (1980).