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The theory of atoms in molecules is extended to the case where the molecule is in the presence of an electromagnetic field. This theory is based upon a generalization of quantum mechanics to an open system, as obtained through a corresponding extension of Schwinger's principle of stationary action. The extension of this principle is possible only if the open system satisfies a particular boundary condition, one which is expressed as a constraint on the variation of the action integral. This is the condition that it be bounded by a surface of zero flux in the gradient vector field of the charge density, the definition of an atom in a molecule. It is shown that this boundary constraint again suffices to define an atom as a quantum subsystem when the molecule is in the presence of an electromagnetic field. The mechanics of an open system and its properties are determined by the fluxes in corresponding vector current densities through its surface. As in the fieldfree case, the obtainment of these currents from the variation of the action integral is a direct result of the variation of the atomic surface and of the imposition of the variational constraint on its boundary. The currents in this case consist of a paramagnetic and a diamagnetic contribution, currents whose presence are a necessary requirement for the description of the properties of a system in the presence of external fields. The variational statement of the Heisenberg equation of motion obtained from the principle of stationary action is used to derive the Ehrenfest force and virial theorems for an atom in a molecule in the presence of external electric and magnetic fields. In this case, there are forces acting on the interior of the atom which arise from the magnetic pressures acting on its surface. It is shown that the molecular electric polarizability and magnetic susceptibility, like other properties, are rigorously expressible as a sum of atomic contributions.

I. INTRODUCTION

There are atoms in molecules and quantum mechanics predicts their properties just as it predicts the properties of the total system.[1,2] The average value of some observable for the total system $\langle \hat{A} \rangle$ is given by the sum of its atomic contributions $A(\Omega)$:

$$\langle \hat{A} \rangle = \Sigma_\Omega A(\Omega). \tag{1}$$

Equation (1) holds for one- and for many-particle operators. It states that each atom in a system makes an additive contribution to the average value of every property that is represented by a linear Hermitian operator. This is the principle underlying the cornerstone of chemistry—that atoms and functional groupings of atoms make recognizable contributions to the total properties of a system. In practice, we recognize a group and predict its effect upon the static and reactive properties of a system in terms of a set of properties assigned to that group. In those limiting situations wherein a group is essentially the same in two different systems, one obtains a so-called additivity scheme for the total properties, for in this case the atomic contributions as well as being additive in the sense of Eq. (1) are transferable between molecules.[3–5] It has been shown that the methyl and methylene groups defined by the theory of atoms in molecules predict the additivity of the energy observed experimentally in normal hydrocarbons. The deviations in this additivity which are found for small cyclic molecules and which serve as the experimental definition of strain energy are also predicted by the theory. The recovery of these experimentally measurable

properties of atoms in molecules confirms that these are the atoms of chemistry. It is the purpose of this paper to demonstrate that the additivity expressed in Eq. (1) also obtains for those properties that are determined by the response of a total system to externally applied electric and magnetic fields. In particular, it is shown that the molecular electric polarizability and the molecular magnetic susceptibility are determined by a sum of atomic contributions in the manner of Eq. (1).

Equation (1) is obtained as a result of a generalization of quantum mechanics to an atom in a molecule.[1] This generalization is accomplished by showing that Schwinger's principle of stationary action,[6] which provides the basis for the quantum mechanical description of a total system, also defines the observables, their average values, and their equations of motion for a particular class of subsystems of a total system. These subsystems satisfy a boundary condition stated in terms of a property of the electronic charge density, that the flux in the gradient vector field of the charge density $\rho(r)$ vanishes at every point of the surface $S(\Omega,r)$ which bounds the subsystem. That is, the surface is one of zero flux in $\nabla\rho$:

$$\nabla\rho(r)\cdot n(r) = 0, \quad \forall r \in S(\Omega,r). \tag{2}$$

Because of the dominant topological property of a molecular charge distribution—that it exhibits local maxima at the positions of the nuclei—the above boundary condition leads to a partitioning of a system into a set of disjoint, mononuclear spatial regions or atoms.[7,8] Each atom behaves as an open

quantum subsystem, free to exchange charge and momentum with the remainder of the system in a manner determined by the atomic principle of stationary action. In order to extend the predictions of this theory of atoms in molecules to situations where external fields act on the system, it must be demonstrated that the principle of stationary action continues to apply to a region of space bounded by a zero flux surface when the molecule is in the presence of an electromagnetic field.

II. PRINCIPLE OF STATIONARY ACTION

Schwinger's *quantum action principle* is a differential equation for the transformation function

$$\delta\langle q_{r2},t_2|q_{r1},t_1\rangle = (i/\hbar)\langle q_{r2},t_2|\delta\widehat{\mathscr{W}}_{12}|q_{r1},t_1\rangle$$

$$= (i/\hbar)\langle q_{r2},t_2|\delta\int_{t_1}^{t_2}\widehat{\mathscr{L}}[t]dt\,|q_{r1},t_1\rangle. \quad (3)$$

This principle embodies Schwinger's postulate that if variations are effected in a quantum mechanical system, the corresponding change in the transformation function between the eigenstates $|q_{r1},t_1\rangle$ and $|q_{r2},t_2\rangle$ is $(i/\hbar)$ times the matrix element of the variation of the action integral $\widehat{\mathscr{W}}_{12}$ connecting the two states. The action integral operator $\widehat{\mathscr{W}}_{12}$ is defined as

$$\widehat{\mathscr{W}}_{12} = \int_{t_1}^{t_2}\widehat{\mathscr{L}}[t]dt, \quad (4)$$

where $\widehat{\mathscr{L}}[t]$, the Lagrange function operator, is an invariant Hermitian function of the field Ψ and its first derivatives. The *principle of stationary action* is obtained from Eq. (3) by noting that an infinitesimal unitary transformation can also be used to obtain a differential characterization of a transformation function. The operator $\widehat{U}$:

$$\widehat{U} = \widehat{1} - (i\epsilon/\hbar)\widehat{G} \quad (5)$$

and its inverse

$$\widehat{U}^{-1} = \widehat{1} + (i\epsilon/\hbar)\widehat{G}, \quad (6)$$

where ϵ denotes an infinitesimal real quantity and $\widehat{G}$ is a linear Hermitian operator, induce infinitesimal unitary transformations. In what follows, $\epsilon\widehat{G}$ will be represented by the infinitesimal unitary operator $\widehat{F}$, where $\widehat{F}$ is referred to as the generator of the transformation. The effect of altering the two commuting sets of position operators at times t_1 and t_2 in the transformation function $\langle q_{r2},t_2|q_{r1},t_1\rangle$ into $\widehat{q}_{r1} - \delta\widehat{q}_{r1}$ and $\widehat{q}_{r2} - \delta\widehat{q}_{r2}$ by the action of the two infinitesimal generating operators $\widehat{F}(t_1)$ and $\widehat{F}(t_2)$ is given by

$$\delta\langle q_{r2},t_2|q_{r1},t_1\rangle = \langle\delta q_{r2},t_2|q_{r1},t_1\rangle + \langle q_{r2},t_2|\delta q_{r1},t_1\rangle$$

$$= (i/\hbar)\langle q_{r2},t_2|\widehat{F}(t_2) - \widehat{F}(t_1)|q_{r1},t_1\rangle. \quad (7)$$

If the parameters of a system are not altered, then the variation of the action integral in Eq. (3) arises only from infinitesimal changes of the sets of commuting observables at the two times t_1 and t_2. However, by Eq. (7), such a transformation is characterized in terms of the generators of infinitesimal unitary transformations $\widehat{F}(t_1)$ and $\widehat{F}(t_2)$ acting on the

two eigenvectors. Thus comparing Eqs. (3) and (7), one obtains for such variations the result

$$\delta\widehat{\mathscr{W}}_{12} = \widehat{F}(t_2) - \widehat{F}(t_1) \quad (8)$$

which is the *operator principle of stationary action*. It states that the action integral operator is unaltered by infinitesimal variations in state functions between the times t_1 and t_2, being affected only by the action of generators at the two time endpoints.

In the principle of stationary action, the variation of the action integral does not vanish as it does in Hamilton's principle, but instead equals the difference in the effects of infinitesimal generators acting at the two time endpoints. This result requires that the variation of the action integral appearing in Eqs. (3) and (8) be generalized to include the variation of the time at the time endpoints and to retain the variations at the endpoints. The principle of stationary action then implies the equation of motion of the system as obtained in Hamilton's principle, and the endpoint variations define the generators of the infinitesimal canonical transformations which induce changes in the dynamical properties of the system. In this way, a single dynamical principle recovers not only the equation of motion, but also defines the observables, their equations of motion and the Heisenberg commutation relations.[9,10]

A number of alternative expressions of the principle of stationary action will prove useful in its application to a subsystem. The first is a restatement of Eq. (8) to give

$$\delta\widehat{\mathscr{W}}_{12} = \int_{t_1}^{t_2}\left(\frac{d\widehat{F}}{dt}\right)dt. \quad (9)$$

By dividing both sides of this equation by $t_2 - t_1$ and subjecting the result to the limit $\Delta t \to 0$, one obtains an expression for the principle of stationary action in terms of a variation of the Lagrange function

$$\delta\widehat{\mathscr{L}}[t] = \frac{d\widehat{F}}{dt}. \quad (10)$$

This result can be equivalently expressed, using Heisenberg's equation for $d\widehat{F}/dt$, as

$$\delta\widehat{\mathscr{L}}[t] = (i/\hbar)[\widehat{H},\widehat{F}], \quad (11)$$

where it is understood that the variation in $\widehat{\mathscr{L}}$ is effected by the action of the infinitesimal generator $\widehat{F}$. Equation (11) is the operational statement of the principle of stationary action. It determines the equations of motion for the observables and the related theorems, such as the Ehrenfest and virial theorems, which determine the mechanics of a given system.

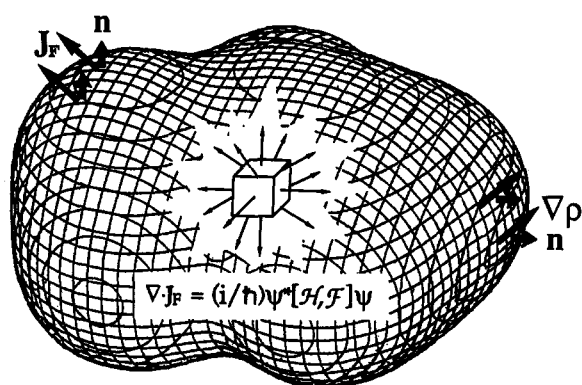## III. ATOMIC PRINCIPLE OF STATIONARY ACTION

The generalization of the principle of stationary action to a subsystem is necessarily stated in the coordinate basis, as the boundary condition in Eq. (2) is defined in real space and the Schrödinger representation of the state vector is employed in what follows. The atomic statement of the principle corresponding to Eq. (11), as previously obtained,[1] is

$$\delta\mathscr{L}[\Psi,\Omega,t] = (1/2)\{(i/\hbar)\langle[\hat{H},\hat{F}]\rangle_\Omega + \mathrm{cc}\}, \quad (12)$$

where the variation in the atomic Lagrangian, the quantity $\delta\mathscr{L}[\Psi,\Omega,t]$, is effected by the action of the generator $\hat{F}$ on the state function Ψ. This equation enables one to obtain a quantum mechanical description of the properties of any region of space bounded by a surface of zero flux in the gradient vector field of the charge density (2). Since a total isolated system satisfies this same boundary condition, Eq. (12) represents a generalization of quantum mechanics.

The definition of an atomic average of some observable is determined by the method of averaging the Lagrangian integral and hence the commutator in the atomic principle of stationary action. Since operators in general are not Hermitian over a subsystem, every property is expressed as an average with its complex conjugate. The non-Hermiticity of the Hamiltonian $\hat{H}$ over a subsystem is of crucial importance, as it results in a net flux in the vector current density through the surface of the subsystem for any observable $\hat{F}$ which is not a constant of the motion. The existence of this current implies in turn that there is a nonvanishing fluctuation in the atomic average of the observable $\hat{F}$.[2] An atom in a molecule is an open system and its properties are determined by fluxes in corresponding vector current densities through its surface (see Fig. 1).

$$\oint dS(\Omega)\, J_F\cdot n + \mathrm{cc} = (i/2\hbar)\langle\psi\,[\mathscr{H},\mathscr{F}]\psi\rangle_\Omega + \mathrm{cc}$$

$$\delta\mathcal{L}[\mathscr{F}\psi,\Omega] = (i/2\hbar)\langle\psi\,[\mathscr{H},\mathscr{F}]\psi\rangle_\Omega + \mathrm{cc}$$

$$\delta\mathcal{G}[\mathscr{F}\psi,\Omega] = -(i/2\hbar)\langle\psi\,[\mathscr{H},\mathscr{F}]\psi\rangle_\Omega + \mathrm{cc}$$

FIG. 1. Even in a stationary state where the time derivative of some property density ρ_F [Eq. (47)] vanishes, there is a net outflow $\nabla\cdot J_F$ of its current density J_F [Eq. (48)] from an infinitesimal region of space. Consequently, there is a net flux in J_F through the surface of an open system Ω equal to the corresponding average of the commutator of the observable $\hat{F}$ with the Hamiltonian $\hat{H}$. If the system is bounded by a surface of zero flux in $\nabla\rho$, i.e., the vector $\nabla\rho$ is tangent to the surface at every point as indicated in the figure, then the flux in J_F through the surface is determined by the variation in the Lagrangian integral $\mathscr{L}[\Psi,\Omega]$ [Eq. (12)] for the time-dependent system, or by the variation in Schrödinger's energy function $\mathscr{G}[\Psi,\Omega]$ [Eq. (52)] for a stationary state. In this case, everything in the diagram is predicted by the principle of stationary action.

It is the purpose of this paper to show that the atomic statement of the principle of stationary action remains true, subject to the same zero flux boundary condition given in Eq. (2), when the molecule containing the atom is in the presence of an electromagnetic field.

A. Properties of the quantum action and Lagrangian integrals

The action integral $\mathscr{W}_{12}[\Psi]$ for the total system is

$$\mathscr{W}_{12}[\Psi] = \int_{t_1}^{t_2}\mathscr{L}[\Psi,t] = \int_{t_1}^{t_2} dt \int d\tau\, L[\Psi,\nabla\Psi,\dot{\Psi},t], \quad (13)$$

where the Lagrangian integral $\mathscr{L}[\Psi,t]$ is obtained by integration of the Lagrangian density over the coordinates of all the particles in the system. In the absence of external fields, the Lagrangian density for a system of many particles interacting via a many-particle potential energy operator $\hat{V}$ is

$$L[\Psi,\nabla\Psi,\dot{\Psi},t]$$
$$= (i\hbar/2)(\Psi^*\dot{\Psi} - \dot{\Psi}^*\Psi) - (\hbar^2/2m)\Sigma_i\nabla_i\Psi^*\cdot\nabla_i\Psi$$
$$- \hat{V}\Psi^*\Psi. \quad (14)$$

The variation to first-order of this action integral with respect to the independent variables Ψ and Ψ^* and with $\delta\Psi$ and $\delta\Psi^* = 0$ at the time endpoints, yields for the extremum condition that $\delta W_{12} = 0$, Schrödinger's equations

$$i\hbar\dot{\Psi} = \hat{H}^0\Psi \quad \text{and} \quad -i\hbar\dot{\Psi}^* = \hat{H}^0\Psi^*, \quad (15)$$

where the Hamiltonian $\hat{H}^0$ is given by

$$\hat{H}^0 = -(\hbar^2/2m)\Sigma_i\nabla_i^2 - \Sigma_i\Sigma_\alpha Z_\alpha e^2(|\mathbf{r}_i - \mathbf{X}_\alpha|)^{-1}$$

$$+ \sum_{i<j}\sum e^2(|\mathbf{r}_i - \mathbf{r}_j|)^{-1}$$

$$+ \sum_{\alpha<\beta}\sum e^2 Z_\alpha Z_\beta(|\mathbf{X}_\alpha - \mathbf{X}_\beta|)^{-1}. \quad (16)$$

Terms of the form $\nabla\Psi^*\cdot\mathbf{n}\delta\Psi$ appear in an integral over the surface of the system when an integration by parts is used to rid the variation in $\mathscr{W}_{12}$ of terms of the form $\delta\nabla\Psi$. Thus to obtain Eqs. (15) as the Euler equations in the variation of the action integral requires that one either demand that $\delta\Psi$ vanish on the boundaries of the system at infinity, or that the state function satisfies the so-called natural boundary conditions that $\nabla\Psi\cdot\mathbf{n} = 0$ and $\nabla\Psi^*\cdot\mathbf{n} = 0$ on the same infinite boundaries.[11]

The Lagrangian density and the integrals it defines exhibit an important property at the point of variation where Schrödinger's equations hold. Denoting by L^0 the Lagrangian density obtained at the point of variation, one has, using Eqs. (15),

$$L^0 = -(\hbar^2/4m)\Sigma_i\{\Psi^*\nabla_i^2\Psi + \Psi\nabla_i^2\Psi^* + 2\nabla_i\Psi^*\cdot\nabla_i\Psi\}. \quad (17)$$

This can be further simplified using the following identity which relates the kinetic energy as it appears in Schrödinger's equation with that appearing in the Lagrangian:

$$- (\hbar^2/4m)\Sigma_i\{\Psi^*\nabla_i^2\Psi + \Psi\nabla_i^2\Psi^*\}$$
$$= (\hbar^2/2m)\Sigma_i\nabla_i\Psi^*\cdot\nabla_i\Psi$$
$$- (\hbar^2/4m)\Sigma_i\nabla_i^2(\Psi^*\Psi). \qquad (18)$$

Thus at the point of variation, the Lagrangian density reduces to a sum of single-particle Laplacian operators acting on $\Psi^*\Psi$:

$$L^0 = - (\hbar^2/4m)\Sigma_i\nabla_i^2(\Psi^*\Psi). \qquad (19)$$

Integration of this quantity over the coordinates of the particles causes it to vanish since the integration reduces to surface integrals of $\nabla\Psi^*\cdot\mathbf{n}$ and $\nabla\Psi\cdot\mathbf{n}$. Thus the Lagrangian integral at any time t and its associated action integral for any time interval Δt for a quantum mechanical system described by Schrödinger's equation must vanish. Because of the single-particle nature of the operator in Eq. (19), one can define a related single-particle density $\mathscr{L}^0(\mathbf{r},t)$. This is accomplished by a summation over the spins of all the electrons, followed by an integration over all coordinates but those of one electron, a process denoted by the symbol $\int d\tau'$. When this result is multiplied by N, the number of electrons in the system, this is the same procedure used to obtain the charge density from $\Psi^*\Psi$. The density obtained in this manner is

$$\mathscr{L}^0(\mathbf{r},t) = \int d\tau' L^0 = - (\hbar^2/4mN)\nabla^2\rho(\mathbf{r},t). \qquad (20)$$

Because of the natural boundary condition that $\Psi^*\nabla\Psi\cdot\mathbf{n}$ and $\Psi\nabla\Psi^*\cdot\mathbf{n}$ vanish on the boundaries of the system at infinity, the vanishing of the Lagrangian integral $\mathscr{L}^0[\Psi,t]$ can be taken to be a consequence of the vanishing of the flux in the gradient vector field of the charge density at the infinite boundary of the system, since

$$\mathscr{L}^0[\Psi,t] = - (\hbar^2/4mN)\int d\tau\, \nabla^2\rho(\mathbf{r},t)$$
$$= - (\hbar^2/4mN)\oint dS(\mathbf{r},t)\nabla\rho(\mathbf{r},t)\cdot\mathbf{n}(\mathbf{r},t) = 0. \qquad (21)$$

The atomic Lagrangian integral is obtained from the Lagrangian density in Eq. (14) by the summing of spins and integration over the coordinates of all electrons but one, followed by the integration of the final electronic coordinate, denoted by $\mathbf{r}$, over the basin of the atom Ω, as indicated in Eq. (22):

$$\mathscr{L}[\Psi,\Omega,t] = \int_\Omega d\mathbf{r}\int d\tau'\, L(\Psi,\nabla\Psi,\dot\Psi,t). \qquad (22)$$

Correspondingly, the atomic action integral is

$$\mathscr{W}_{12}[\Psi,\Omega] = \int_{t_1}^{t_2} dt\, \mathscr{L}[\Psi,\Omega,t]. \qquad (23)$$

The generalized variation of the atomic action integral *and including a variation of the surface bounding the atom*, yields the atomic statements of the quantum action principle and principle of stationary action if one imposes a particular variational constraint. This constraint amounts to delimiting the class of possible subsystems to those which satisfy the zero flux surface condition given in Eq. (2). The manner in which this constraint is imposed is illustrated in the deriva-

tion of the action principle for an atom in the presence of an electromagnetic field.

B. Atoms in an electromagnetic field

We choose a gauge for the scalar and vector potentials of the electromagnetic field, designated by $\phi(\mathbf{r})$ and $\mathbf{A}(\mathbf{r})$, respectively, in which $\nabla\cdot\mathbf{A} = 0$. This choice has the consequence of causing $\mathbf{A}$ and the momentum operator $\hat{\mathbf{p}}$ to commute. In the presence of an electromagnetic field, the momentum operator $\hat{\mathbf{p}}$ is replaced by the expression

$$\hat{\boldsymbol\pi} = \hat{\mathbf{p}} - (e/c)\mathbf{A}(\mathbf{r},t) \qquad (24)$$

for a particle of charge e. Through the use of Eq. (24) and the inclusion of the scalar potential ϕ, the many-particle Lagrangian density given in Eq. (24) can be modified for the presence of external electric and magnetic fields. This modified Lagrangian $L(\Psi,\nabla\Psi,\dot\Psi,\mathbf{A},\phi)$ can be expressed as

$$L(\Psi,\nabla\Psi,\dot\Psi,\mathbf{A},\phi) = L(\Psi,\nabla\Psi,\dot\Psi) + \frac{i\hbar e}{2mc}\Sigma_i\{\nabla_i\Psi^*\cdot\mathbf{A}(\mathbf{r}_i)\Psi$$
$$- \mathbf{A}(\mathbf{r}_i)\Psi^*\cdot\nabla_i\Psi\} - \frac{e^2}{2mc^2}\Sigma_i A^2(\mathbf{r}_i)\Psi^*\Psi$$
$$- \Sigma_j e_j\phi(\mathbf{r}_j)\Psi^*\Psi, \qquad (25)$$

where the sum j runs over all the charged particles in the system. The associated action integral is defined as

$$\mathscr{W}_{12}[\Psi,\mathbf{A},\phi] = \int_{t_1}^{t_2}\int d\tau\, L(\Psi,\nabla\Psi,\dot\Psi,\mathbf{A}\phi)dt. \qquad (26)$$

Variation of the action integral with respect to Ψ^* subject to the natural boundary condition that $\nabla_i\Psi\cdot n = 0$ on the surface at infinity and with the condition that the variations in Ψ^* vanish at the time endpoints, yields Schrödinger's equation for a system in the presence of an electromagnetic field

$$i\hbar\dot\Psi = \frac{1}{2m}\Sigma_i\left(\frac{\hbar}{i}\nabla_i - \frac{e}{c}\mathbf{A}(\mathbf{r}_i)\right)^2\Psi + (\widehat{V} + \Sigma_j e_j\phi(\mathbf{r}_j))\Psi. \qquad (27)$$

This result may be reexpressed in terms of $\widehat{H}^0$, the usual fieldfree Hamiltonian as given in Eq. (16) and an interaction Hamiltonian $\widehat{H}^i$ as

$$i\hbar\dot\Psi = \widehat{H}^0\Psi + \widehat{H}^i\Psi, \qquad (28)$$

where $\widehat{H}^i$ is given by

$$\widehat{H}^i = - \frac{e}{2mc}\Sigma_i(\hat{\mathbf{p}}_i\cdot\mathbf{A}(\mathbf{r}_i) + \mathbf{A}(\mathbf{r}_i)\cdot\hat{\mathbf{p}}_i) + \frac{e^2}{2mc^2}\Sigma_i A^2(\mathbf{r}_i)$$
$$+ \Sigma_j e_j\phi(\mathbf{r}_j). \qquad (29)$$

It is easily verified that when Schrödinger's Eq. (27) is satisfied, the many-particle Lagrangian in the presence of the external fields as given in Eq. (25) still reduces to a sum of terms, each of which is proportional to the Laplacian operator for a single electron acting on the product $\Psi^*\Psi$ as obatined in Eq. (19) for the fieldfree case. Thus

$$L^0(\Psi,\nabla\Psi,\dot\Psi,\mathbf{A},\phi) = (-\hbar^2/4m)\Sigma_i\nabla_i^2(\Psi^*\Psi). \qquad (30)$$

It is through this property of the Lagrangian that the consequences of the variational constraint which demands that the subsystem be bounded by a surface of zero flux in the gradient vector field of ρ is incorporated into the variation of the atomic action integral.

In analogy with Eq. (22), the atomic Lagrangian integral in the presence of external fields is defined as

$$\mathcal{L}[\Psi,\Omega,\mathbf{A},\phi,t] = \int_\Omega d\mathbf{r} \int d\tau' \, L(\Psi,\nabla\Psi,\dot{\Psi},\mathbf{A},\phi)$$

$$= \int_\Omega d\mathbf{r} \, \mathcal{L}(\mathbf{r},\mathbf{A},\phi) \tag{31}$$

and the associated action integral as

$$\mathcal{W}_{12}[\Psi,\Omega,\mathbf{A},\phi] = \int_{t_1}^{t_2} dt \, \mathcal{L}[\Psi,\Omega,\mathbf{A},\phi,t]. \tag{32}$$

At the point of variation, where Ψ and Ψ^* satisfy Schrödinger's equation, the atomic Lagrangian integral because of Eq. (30) reduces to a surface integral of the flux in $\nabla\rho$ through the surface of the subsystem

$$\mathcal{L}^0[\Psi,\Omega,\mathbf{A},\phi,t] = \int_\Omega d\mathbf{r} \, \mathcal{L}^0(\mathbf{r},A,\phi)$$

$$= -(\hbar^2/4mN)\int_\Omega d\mathbf{r} \, \nabla^2\rho(\mathbf{r},t)$$

$$= -(\hbar^2/4mN)\oint dS(\Omega,t)\nabla\rho(\mathbf{r},t)\cdot\mathbf{n}(\mathbf{r},t). \tag{33}$$

Thus the atomic Lagrangian and action integrals in the presence of an electromagnetic field, like their fieldfree counterparts, vanish as a consequence of the zero flux surface condition (2). These properties are common to the corresponding integrals for the total system [Eq. (21)] and it is a consequence of this equivalence in properties that the action integrals for the total system and each of the atoms which comprise it have similar variational properties.

The definition of an atom in a molecule in the presence of an electromagnetic field is accomplished by defining its properties using the principle of stationary action. This principle for a total system and for an atom within the system are obtained as in the fieldfree case through a variation of the corresponding action integrals, where the variation is generalized to include a variation of the time endpoints and by the retention of the variations in the state function at the time endpoints. It is the endpoint variations that are identified with the generators of infinitesimal unitary transformations. In this manner, the change in the action integral is equated to

the action of infinitesimal unitary transformations acting on the state functions at the two time endpoints, a relationship known as the principle of stationary action. At every stage of the variation of the atomic action integral, which includes a variation of its surface, the variation is subject to the following conditions[1]:

(i) The trial function Φ, where $\Phi = \Psi + \delta\Psi$, and its first derivative vanish whenever an electronic position vector is of infinite length.

(ii) In terms of Φ, a region $\Omega(\Phi,t)$ can be defined that is bounded by a zero flux surface in $\nabla\rho_\Phi$:

$$\nabla\rho_\Phi(\mathbf{r},t)\cdot\mathbf{n}(\mathbf{r},t) = 0, \quad \text{for all points on the surface of } \Omega, \tag{34}$$

where the trial density is defined as

$$\nabla\rho_\Phi(\mathbf{r},t) = N\int d\tau' \, \Phi^*(\mathbf{r},\tau',t)\Phi(\mathbf{r},\tau',t). \tag{35}$$

Moreover, it is required that as Φ tends to Ψ at any time t, $\Omega(\Phi,t)$ is continuously deformable into the region $\Omega(t) = \Omega(\Psi,t)$ associated with the atom. The region $\Omega(\Phi,t)$ thus represents the atom in the varied total system, which is described by trial function $\Phi(\mathbf{r},\tau',t)$ just as $\Omega(\Psi,t)$ represents the atom when the total system is in the state described by $\Psi(\mathbf{r},\tau',t)$.

Requiring the fulfillment of condition (ii) amounts to imposing the variational constraint that the divergence of $\nabla\rho_\Phi$ integrate to zero at all stages of the variation, i.e., that

$$I_\Phi = \int_{\Omega(\phi,t)} \nabla^2\rho_\Phi \, d\mathbf{r} = 0 \tag{36}$$

for all admissible Φ and for all t, which implies

$$\delta I_\Psi = \delta\left\{\int_{\Omega(t)} \nabla^2\rho(\mathbf{r},t)d\mathbf{r}\right\} = 0. \tag{37}$$

To impose the variational constraint given in Eq. (37) and thereby define a particular class of open system, one must vary the surface of the subsystem. This requirement necessarily leads to the relaxation of the usual variational constraint that $\delta\Psi$ vanish at all boundaries of the system and at the time endpoints as is done in the restricted variation of the action integral in Hamilton's principle to obtain the equations of motion. *Thus the variation of the atomic action integral with the necessary retention of $\delta\Psi$ on the boundaries and hence at the time endpoints perforce leads to the generalization of the variation of the action integral that yields Schwinger's principle of stationary action.*

The result of such a generalized variation of the atomic action integral given in Eq. (32) is

$$\delta\mathcal{W}_{12}[\Psi,\Omega,\mathbf{A},\phi] = \int_{t_1}^{t_2} dt \int_\Omega d\mathbf{r} \int d\tau'\{(-i\hbar\dot{\Psi}^* - \hat{H}^0\Psi^* - \hat{H}^i\Psi^*)\delta\Psi + \text{cc}\}$$

$$+ \int_{t_1}^{t_2} dt \oint dS(\Omega,\mathbf{r}) \int d\tau'(-\hbar^2/2m)\left\{\left(\nabla\Psi^* + \frac{ie}{\hbar c}\mathbf{A}(\mathbf{r})\Psi^*\right)\delta\Psi\cdot\mathbf{n}(\mathbf{r}) + \text{cc}\right\}$$

$$+ \int_{t_1}^{t_2} dt \oint dS(\Omega,\mathbf{r})\left\{\mathcal{L}^0(\mathbf{r},A,\phi)\delta S(\Omega,\mathbf{r}) + \int d\tau'(-i\hbar/2)\left(\frac{\partial S(\Omega,\mathbf{r})}{\partial t}\right)\Psi^*\delta\Psi + \text{cc}\right\}$$

$$+ \left\{(i\hbar/2)\int_\Omega d\mathbf{r} \int d\tau' \, \Psi^*\delta\Psi + \text{cc}\right\}\Big|_{t_1}^{t_2}. \tag{38}$$

The first set of terms multiplying the variations in Ψ and the corresponding complex conjugate set yield Schrödinger's equations for Ψ and Ψ^* [Eq. (27)] for the case of the restricted variation; i.e., where the natural boundary conditions are imposed, the endpoint variations are set equal to zero and Ω equals all space. The equations of motion are thus obtained for the total system and are assumed from this point on {they are in any case implied by the principle of stationary action [Eq. (8)]}. Since the Lagrangian integral vanishes at the point of variation, its contribution to the change in action at the time endpoints has been omitted. The Lagrangian density at the point of variation $\mathscr{L}^0(\mathbf{r},\mathbf{A},\phi)$ appearing in the second of the surface terms multiplied by the variation in the surface of the subsystem is defined in Eq. (33) and is seen to be proportional to the Laplacian of the charge density. It is through this term that the variational constraint as given in Eq. (37) is incorporated into the expression for the variation of the atomic action integral. The imposition of the variational constraint is accomplished using the identity given in Eq. (39). This result is obtained when one carries out the variation of the Laplacian integral for the region Ω including a variation of its surface[11] as demanded in Eq. (37)

$$\delta\left\{(\hbar^2/4mN)\int_\Omega dr\,\nabla^2\rho(\mathbf{r})\right\}$$

$$= (\hbar^2/4mN)\int_\Omega d\mathbf{r}\,\delta\{\nabla^2\rho(\mathbf{r})\} + (\hbar^2/4mN)\oint dS(\Omega,\mathbf{r})$$

$$\times\nabla^2\rho(\mathbf{r})\delta S(\Omega,\mathbf{r}). \qquad (39)$$

The variation of the integrand as indicated in Eq. (39) is given in Eq. (40):

$$\int_\Omega \delta\{\nabla^2\rho(\mathbf{r})\}d\tau = N\int_\Omega d\mathbf{r}\int d\tau'\{\nabla^2\Psi^*\delta\Psi + 2\nabla\Psi^*\cdot\delta\nabla\Psi$$

$$+ \Psi^*\delta\nabla^2\Psi\} + \text{cc}$$

$$= N\int_\Omega d\mathbf{r}\int d\tau'\,\nabla\cdot\{\nabla\Psi^*\delta\Psi$$

$$+ \Psi^*\nabla\delta\Psi\} + \text{cc}. \qquad (40)$$

The Laplacian is a divergence expression—its variation yields only surface terms—and through Green's theorem, the final term in Eq. (40) yields the surface integral on the right-hand side of Eq. (41). Thus the imposition of the constraint does not affect the Euler–Lagrange equations that have been obtained at this point. According to the constraint (37), the sum of variations of the integrand and surface must equal zero and thus the result of imposing the constraint is to replace the surface variation with the term arising from the variation of $\nabla^2\rho(r)$ as shown in Eq. (41):

$$-(\hbar^2/4mN)\oint dS(\Omega,\mathbf{r})\nabla^2\rho(\mathbf{r})\delta S(\Omega,\mathbf{r})$$

$$= (\hbar^2/4m)\oint dS(\Omega,\mathbf{r})\int d\tau'\{(\nabla\Psi^*)\delta\Psi$$

$$+ \Psi^*\delta\nabla\Psi\}\cdot\mathbf{n}(\mathbf{r}) + \text{cc}. \qquad (41)$$

Substitution of the result given for the variation of the Laplacian in Eq. (41) for the surface variation term into Eq. (38)

together with the use of Schrödinger's Eq. (27) yields the following expression for the variation of the atomic action integral:

$$\delta\mathscr{W}_{12}[\Psi,\Omega,\mathbf{A},\phi] = \int_{t_1}^{t_2} dt \oint dS(\Omega,\mathbf{r})\,(i\hbar/2)\Big\{\delta_\Psi\mathbf{j}_B(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})$$

$$+ \text{cc} - \int d\tau'\left(\frac{\partial S}{\partial t}\right)\Psi^*\delta\Psi + \text{cc}\Big\}$$

$$+ (i\hbar/2)\int_\Omega d\mathbf{r}\int d\tau'\Psi^*\delta\Psi + \text{cc}\Big|_{t_1}^{t_2}. \qquad (42)$$

The quantity $\mathbf{j}_B$ is the vector current density for a particle in the presence of a magnetic field $\mathbf{B} = \nabla\times\mathbf{A}$ and it is defined as

$$\mathbf{j}_B(\mathbf{r}) = \mathbf{j}(\mathbf{r}) - (e/mc)\rho'(\mathbf{r})\mathbf{A}(\mathbf{r})$$

$$= (\hbar/2mi)\int d\tau'[\Psi^*\nabla\Psi - \nabla\Psi^*\Psi]$$

$$- (e/mc)\int d\tau'\,\Psi^*\Psi\mathbf{A}(\mathbf{r}). \qquad (43)$$

The first term $\mathbf{j}(r)$ is the usual vector current density and its variation $\delta_\Psi\mathbf{j}(\mathbf{r})$ as it appears in Eq. (42) is

$$\delta_\Psi\mathbf{j}(\mathbf{r}) = (\hbar/2mi)\int d\tau'(\Psi^*\delta\nabla\Psi - \nabla\Psi^*\delta\Psi). \qquad (44)$$

This term is obtained by combining the surface term in Eq. (38) arising from the variations with respect to $\nabla\Psi$, with the surface term arising from the imposition of the variational constraint (41). *Thus the variation of the surface of the subsystem together with the restriction that the subsystem be an atom bounded by a zero flux surface causes the quantum mechanical current density* $\mathbf{j}_B$ *to appear in the variation of the action integral,* a term whose presence is a necessary requirement for the description of the properties of an open system. The second term in $\mathbf{j}_B$ owes its existence to the presence of a magnetic field and is simply the charge density $\rho(\mathbf{r})$ multiplied by the vector potential $\mathbf{A}$. The two terms are called the paramagnetic and diamagnetic currents, respectively.

Proceeding as in the fieldfree case, the variations in the state function are replaced by operators which act as generators of infinitesimal unitary transformations. That is, $\delta\Psi = (-i/\hbar)\widehat{F}\Psi$, where $\widehat{F}$ is an infinitesimal Hermitian operator $(\widehat{F} = \epsilon\widehat{G})$. Introducing the notion of generators into the result for the variation of the atomic action integral yields

$$\Delta\mathscr{W}_{12}[\Psi,\Omega,\mathbf{A},\phi] = F(\Omega,t_2) - F(\Omega,t_1)$$

$$- \int_{t_1}^{t_2} dt \oint dS(\Omega,\mathbf{r})\left\{\left(\frac{\partial S}{\partial t}\right)\rho_F\right.$$

$$\left. - [\mathbf{J}_F^d(\mathbf{r}) + \tfrac{1}{2}(\mathbf{J}_F(\mathbf{r}) + \text{cc})]\cdot\mathbf{n}(\mathbf{r})\right\}. \qquad (45)$$

The result is expressed in terms of property averages for N electrons, so $\Delta\mathscr{W} = N\delta\mathscr{W}$. The atomic averages of the generator at the time endpoints $F(\Omega,t)$ and the corresponding property density ρ_F are defined as

$$F(\Omega,t) = \int_\Omega d\mathbf{r}\, \rho_F(\mathbf{r},t)$$

$$= (N/2) \int_\Omega d\mathbf{r} \int d\tau' \{\Psi^* \widehat{F}\Psi + (\widehat{F}\Psi)^*\Psi\} \qquad (46)$$

and

$$\rho_F(\mathbf{r},t) = (N/2) \int d\tau' \{\Psi^* \widehat{F}\Psi + (\widehat{F}\Psi)^*\Psi\}. \qquad (47)$$

The paramagnetic contribution to the magnetic current density for the observable $\widehat{F}$ is

$$\mathbf{J}_F(\mathbf{r},t) = (N\hbar/2mi) \int d\tau' \{\Psi^*\nabla(\widehat{F}\Psi) - (\nabla\Psi^*)\widehat{F}\Psi\}. \qquad (48)$$

The diamagnetic contribution to the total magnetic current density for property F is given by

$$\mathbf{J}_F^d(\mathbf{r}) = -(e/mc)\rho_F(\mathbf{r})\mathbf{A}(\mathbf{r}). \qquad (49)$$

To reexpress the result given for $\Delta\mathcal{W}$ in Eq. (45) in the form analogous to Eq. (9), we need the Heisenberg equation of motion for $F(\Omega,t)$ in the presence of a magnetic field. This is obtained using Eq. (27) for Schrödinger's equation of motion to give

$$\frac{dF(\Omega,t)}{dt} = (\tfrac{1}{2})\{(i/\hbar)\langle[\widehat{H},\widehat{F}]\rangle_\Omega + \mathrm{cc}\}$$

$$+ \oint dS(\Omega,\mathbf{r})\left\{\left(\frac{\partial S}{\partial t}\right)\rho_F - [\mathbf{J}_F^d(\mathbf{r})\right.$$

$$\left. + \tfrac{1}{2}(\mathbf{J}_F(\mathbf{r}) + \mathrm{cc})]\cdot\mathbf{n}(\mathbf{r})\right\}. \qquad (50)$$

Comparison of this expression with that for the change in action in Eq. (45) shows that the terms subtracted from the endpoint averages of the generator are just those which account for the surface contributions to this difference integrated over the timelike surface connecting the two time endpoints. Thus, what remains is the difference in the values of the generator at the two time endpoints averaged over the interior of the subsystem, the essence of the principle of stationary action.[1] As in the fieldfree case, the change in the atomic action integral can be expressed entirely in terms of the interior averages of the generator as

$$\Delta W_{12}[\Psi,\Omega,\mathbf{A},\phi] = \int_{t_1}^{t_2} dt\{(i/\hbar)\langle[\widehat{H},\widehat{F}]\rangle_\Omega + \mathrm{cc}\}/2, \qquad (51)$$

a result equivalent to the statements of stationary action obtained for the total system (9) and for an atom in the absence of an electromagnetic field. The statements for the variation of the Lagrangian in the presence of the field $\delta\mathcal{L}[\Psi,\Omega,\mathbf{A},\phi]$ is identical in form to that given in Eq. (12) for the fieldfree case with the understanding that the Hamiltonian appearing in the commutator is the one given in Eq. (27).

For a stationary state, the Lagrangian integral, apart from the presence of a Lagrange multiplier to insure normalization of ψ, reduces to the energy functional used by Schrödinger[12(a)] in the derivation of the stationary state wave equation. For an atom in a molecule in a stationary state with or without externally applied fields, the atomic state-

ment of the stationary action in terms of this functional $\mathcal{G}[\psi]$ is[13]

$$\delta\mathcal{G}[\psi,\Omega] = -\tfrac{1}{2}\{(i/\hbar)\langle[\widehat{H},\widehat{F}]\rangle_\Omega + \mathrm{cc}\}. \qquad (52)$$

The derivation of the principle of stationary action for an atom in a molecule in the time-dependent case or in a stationary state, in the presence or absence of an electromagnetic field, yields the corresponding Schrödinger equation of motion for the total system, identifies the observables with the variations of the state function, defines their average values, and gives their equations of motion. The statements of the atomic principle of stationary action as expressed in terms of variations in $\mathcal{L}[\Psi,\Omega]$ and $\mathcal{G}[\Psi,\Omega]$, are variational statements of Heisenberg's equation of motion and of the hypervirial theorem for a generator $\widehat{F}$, respectively. They yield the theorems and relations governing the mechanics of an atom in a molecule. This is demonstrated here by determining the Ehrenfest force acting on an atom in a molecule in the presence of an electromagnetic field and the corresponding statement of the atomic virial theorem.

IV. ATOMIC FORCE AND VIRIAL THEOREMS IN THE PRESENCE OF EXTERNAL FIELDS

The Hamiltonian in Eq. (27) for a system of electrons of charge $-e$, and nuclei with charge $+Z_\alpha e$ to be used in the principle of stationary action [Eq. (12)] is

$$\widehat{H} = \Sigma_i\{\pi_i^2/2m - \Sigma_\alpha Z_\alpha e^2(|\mathbf{X}_\alpha - \mathbf{r}_i|)^{-1} - e\phi(\mathbf{r}_i)\} + \Sigma_i$$

$$< \Sigma_j e^2(|\mathbf{r}_i - \mathbf{r}_j|)^{-1} + \Sigma_\alpha < \Sigma_\beta Z_\alpha Z_\beta e^2(|\mathbf{X}_\alpha - \mathbf{X}_\beta|)^{-1}$$

$$+ \Sigma_\alpha Z_\alpha e\phi(\mathbf{X}_\alpha)$$

$$= \Sigma_i\widehat{T}_{\pi i} + \widehat{V} + \Phi, \qquad (53)$$

where the momentum operator $\hat{\pi}_i$ is given by

$$\hat{\pi}_i = \hat{\mathbf{p}}_i + (e/c)\mathbf{A}(\mathbf{r}_i) \qquad (54)$$

and where the potential energy contributions have been separated into the normal fieldfree term $\widehat{V}$ and another term Φ containing the effects of the external field ϕ. One may determine the variation in the atomic Lagrangian by subjecting the state function to the infinitesimal unitary transformation generated by the operator $\widehat{F}$. This procedure has been previously illustrated in the derivation of the atomic force law and the atomic virial theorem.[1] However, the variation of the functional can be evaluated in a simpler manner by using the expression obtained prior to the use of the Heisenberg equation of motion to relate it to the commutator. Thus the expression for the variation of the atomic action integral given in Eq. (45), when divided by the time difference $\Delta t = t_2 - t_1$ and taken to the limit of $\Delta t \to 0$ yields an alternative expression for the variation of the atomic Lagrangian

$$\delta\mathcal{L}[\Psi,\Omega,\mathbf{A},\phi] = \frac{dF(\Omega)}{dt} - \oint dS(\Omega,\mathbf{r})\left\{\left(\frac{\partial S}{\partial t}\right)\rho_F\right.$$

$$\left. - [\mathbf{J}_F^d(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) + \tfrac{1}{2}(\mathbf{J}_F(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) + \mathrm{cc})]\right\}. \qquad (55)$$

Note that this result is given for the general case of a particle of charge e, as is done throughout the general derivation.

When used in conjunction with the electronic Hamiltonian in Eq. (53) to obtain expressions for the electronic force and virial, the charge must be replaced by $-e$. Equating the results for $\delta\mathcal{L}$ in Eqs. (12) and (55) is equivalent to using the Heisenberg equation of motion (50) for the generator $\widehat{F}$. However, the equating of the two separate expressions emphasizes that the results are obtained from a variational expression, the atomic statement of the principle of stationary action, one that is restricted to subsystems which satisfy the zero flux boundary condition.

As has been stressed previously,[1,13] the mode of integration used to define the atomic Lagrangian determines the definition of the average value of an atomic property. The coordinate vector appearing in the generator $\widehat{F}$ of the action principle and denoted by the position vector $\mathbf{r}$ is that of the electron whose coordinates are integrated over the basin of the atom, the coordinates of the remaining electrons being integrated over all space and the spins of all electrons summed.[14]

A. Atomic force law

Ehrenfest's fist relation, the definition of the velocity and its associated momentum, is determined by the commutator of $\widehat{H}$ and the position vector $\hat{\mathbf{r}}$. This commutator, using the above Hamiltonian and multiplied by m, does indeed yield $\hat{\boldsymbol{\pi}}$ as the momentum of an electron in an electromagnetic field

$$m(i/\hbar)[\widehat{H},\hat{\mathbf{r}}] = \tfrac{1}{2}(i/\hbar)[\hat{\pi}^2,\hat{\mathbf{r}}] = \hat{\boldsymbol{\pi}}. \tag{56}$$

The atomic statement of the Ehrenfest force law is obtained by setting the generator $\widehat{F}$ equal to the momentum $\hat{\boldsymbol{\pi}}$. The commutator of the many-particle Hamiltonian (53) and $\hat{\boldsymbol{\pi}}$ can be expressed as

$$(i/\hbar)[\widehat{H},\hat{\boldsymbol{\pi}}] = (i/\hbar)[\widehat{V} - e\phi(\mathbf{r}),\hat{\mathbf{p}}] + (i/2m\hbar)[\hat{\pi}^2,\hat{\boldsymbol{\pi}}], \tag{57}$$

where $\widehat{V}$ represents the potential energy contributions from just the internal electric fields, as defined in Eq. (53). All of the potential energy terms commute with the vector potential $\mathbf{A}(\mathbf{r})$. The first of the commutators in the right-hand side of Eq. (57) gives the force exerted on the electron at $\mathbf{r}_1 = \mathbf{r}$ by the nuclei, the other electrons and the external field $\phi(\mathbf{r}_1)$:

$$(i/\hbar)[\widehat{V} - e\phi(\mathbf{r}),\hat{\mathbf{p}}] = -\nabla\widehat{V} + e\nabla\phi(\mathbf{r}), \tag{58}$$

while the second gives the force exerted on the electron by the magnetic field[15,16]

$$(i/2m\hbar)[\hat{\pi}^2,\hat{\boldsymbol{\pi}}] = -(e/2mc)\{\hat{\boldsymbol{\pi}}\times\mathbf{B} - \mathbf{B}\times\hat{\boldsymbol{\pi}}\}. \tag{59}$$

The averaging of the commutators in Eq. (58) and (59), as required by Eq. (12) and multiplication by N, gives the force exerted on the electrons in the atom Ω, a quantity denoted by $F(\Omega,\mathbf{B},\phi,t)$

$$F(\Omega,\mathbf{B},\phi,t) = \frac{N}{2}\{(i/\hbar)\langle[\widehat{H},\hat{\boldsymbol{\pi}}]\rangle + \text{cc}\}$$

$$= \langle -\nabla\widehat{V}\rangle_\Omega + \langle e\nabla\phi(\mathbf{r})\rangle_\Omega$$

$$- (e/4mc)\{\langle(\hat{\boldsymbol{\pi}}\times\mathbf{B} - \mathbf{B}\times\hat{\boldsymbol{\pi}})\rangle_\Omega + \text{cc}\}, \tag{60}$$

where $\langle -\nabla\widehat{V}\rangle_\Omega$ is the force in the absence of external fields and the remaining terms give the atomic averages of the contributions of the external electric and magnetic fields to the Ehrenfest force.

This result is to be equated to the time rate of change of $\hat{\boldsymbol{\pi}}$ and the flux in its paramgnetic and diamagnetic currents through the surface of the atom using Eq. (55). Thus the forces exerted on the electrons in an atom Ω arising from the electric fields within and external to the molecule and from an external magnetic field are equivalently expressed as

$$F(\Omega,\mathbf{B},\phi,t) = m\langle(\partial\mathbf{J}_\pi/\partial t)\rangle_\Omega - \oint dS(\Omega,\mathbf{r})\sigma(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})$$

$$+ \frac{e}{c}\oint dS(\Omega,\mathbf{r})\Big[\{\mathbf{A}(\mathbf{r})\mathbf{J}(\mathbf{r}) + \mathbf{J}(\mathbf{r})\mathbf{A}(\mathbf{r})\}$$

$$+ \frac{e}{mc}\rho(\mathbf{r})\mathbf{A}(\mathbf{r})\mathbf{A}(\mathbf{r})\Big]\cdot\mathbf{n}(\mathbf{r}), \tag{61}$$

where $\sigma(\mathbf{r})$ is the quantum mechanical stress tensor[12(b),17]

$$\sigma(\mathbf{r}) = \frac{N\hbar^2}{4m}\int d\tau'\{\nabla(\nabla\Psi^*)\Psi$$

$$+ \Psi^*\nabla(\nabla\Psi) - \nabla\Psi^*\nabla\Psi - \nabla\Psi\nabla\Psi^*\}. \tag{62}$$

In the absence of external fields, the surface integral of the stress tensor and the atomic average of the time rate of change of the current density $\mathbf{J}(\mathbf{r})$ determine the force.[18] The stress tensor has the dimensions of an energy density, i.e., of a force per unit area or a pressure and the force acting on the interior of the atom is given by the integral of the pressure acting on each of its surface elements. A current density and $(e/mc)\mathbf{A}\rho$ both have the dimensions of a velocity density and their multiplication by $(e/c)\mathbf{A}$, as occurs in Eq. (61), converts them into energy densities or pressures. Thus the final surface term appearing in the atomic force law measures the contribution to the force acting on the interior of the atom that results from the paramagnetic and diamagnetic pressures acting on its surface.

For a stationary state of a system in the presence of uniform external fields, the expression for the force becomes

$$F(\Omega,\mathbf{B},\phi) = \langle -\nabla\widehat{V}\rangle_\Omega + \langle e\nabla\phi(\mathbf{r})\rangle_\Omega$$

$$- (e/4mc)\{\langle(\hat{\boldsymbol{\pi}}\times\mathbf{B} - \mathbf{B}\times\hat{\boldsymbol{\pi}})\rangle_\Omega + \text{cc}\}. \tag{63}$$

These interior forces are generated in their entirety by the mechanical and magnetic pressures acting on the atom's surface as described in Eq. (64):

$$F(\Omega,\mathbf{B},\phi) = -\oint dS(\Omega,\mathbf{r})\sigma(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})$$

$$+ \frac{e}{c}\oint dS(\Omega,\mathbf{r})\Big[\{\mathbf{A}(\mathbf{r})\mathbf{J}(\mathbf{r})$$

$$+ \mathbf{J}(\mathbf{r})\mathbf{A}(\mathbf{r})\} + \frac{e}{mc}\rho(\mathbf{r})\mathbf{A}(\mathbf{r})\mathbf{A}(\mathbf{r})\Big]\cdot\mathbf{n}(\mathbf{r}). \tag{64}$$

As for a stationary state in the absence of fields, Eq. (64) states that the force acting on an atom in a molecule is totally determined by the flux in the forces acting on its surface. The

stress tensor $\sigma(\mathbf{r})$ and the current density $\mathbf{J}(\mathbf{r})$ are both determined by the one-electron density matrix. Thus the information in the one-matrix suffices to determine the mechanics of a system even in the presence of external fields.[18]

B. Atomic virial theorem

The atomic virial theorem for a system in the presence of external fields is obtained by setting the generator $\hat{F}$ equal to $\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\pi}}$. The commutators required for the evaluation of $\delta\mathscr{L}$ [Eq. (12)] are readily evaluated. One has

$$(i/\hbar)[\hat{H},\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\pi}}] = (i/2m\hbar)\{[\pi^2,\hat{\mathbf{r}}]\cdot\hat{\boldsymbol{\pi}} + \mathbf{r}\cdot[\hat{\pi}^2,\hat{\boldsymbol{\pi}}]\} + (i/\hbar)$$
$$\times [V - e\phi(\mathbf{r}),\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\pi}}]. \qquad (65)$$

The results obtained for these commutators parallel those for the fieldfree case. Thus the first commutator yields twice the operator for the kinetic energy, but expressed here in terms of $\hat{\boldsymbol{\pi}}$ [see Eq. (56)]:

$$(i/2m\hbar)[\hat{\pi}^2,\hat{\mathbf{r}}]\cdot\hat{\boldsymbol{\pi}} = \hat{\pi}^2/m = 2\hat{T}_\pi, \qquad (66)$$

while the last yields the virial of the gradient of the potential energy operator $\hat{V}$ and external field $\phi(\mathbf{r})$ with respect to the electron of position vector $\hat{\mathbf{r}}$, the virial of the force operator given in Eq. (58)

$$(i/\hbar)[\hat{V} - e\phi(\mathbf{r}),\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\pi}}] = -\mathbf{r}\cdot\nabla\hat{V} + e\mathbf{r}\cdot\nabla\phi(\mathbf{r}). \qquad (67)$$

The commutator of $\hat{\pi}^2$ with $\hat{\boldsymbol{\pi}}$ gives the magnetic force acting on an electron [Eq. (59)] and the remaining commutator in Eq. (65) gives the virial of this magnetic force

$$(i/2m\hbar)\mathbf{r}\cdot[\hat{\pi}^2,\hat{\boldsymbol{\pi}}] = -\frac{e}{2mc}\mathbf{r}\cdot\{\hat{\boldsymbol{\pi}}\times\mathbf{B} - \mathbf{B}\times\hat{\boldsymbol{\pi}}\}. \qquad (68)$$

The averaging of these commutators in the manner determined by the atomic action principle (12) serves to define the atomic averages of the kinetic energy and of the virials of the internal and external forces acting on the basin of the atom as indicated in Eq. (69):

$$\frac{N}{2}\{(i/\hbar)\langle[\hat{H},\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\pi}}]\rangle_\Omega + \text{cc}\}$$

$$= \langle(\hat{\mathbf{p}} + \frac{e}{c}\mathbf{A}(\mathbf{r}))^2\rangle_\Omega/m + \langle -\mathbf{r}\cdot\nabla\hat{V}\rangle_\Omega + e\langle\mathbf{r}\cdot\nabla\phi(\mathbf{r})\rangle_\Omega - \frac{e}{4mc}\{\langle\mathbf{r}\cdot(\hat{\boldsymbol{\pi}}\times\mathbf{B} - \mathbf{B}\times\hat{\boldsymbol{\pi}})\rangle_\Omega + \text{cc}\}$$

$$= 2T_\pi(\Omega) + \mathscr{V}_b(\Omega) + \mathscr{V}_\phi(\Omega) + \mathscr{V}_B(\Omega). \qquad (69)$$

These contributions are equal to the terms given by the alternative expression for the variation in the atomic Lagrangian for the generator $\hat{\mathbf{r}}\cdot\hat{\boldsymbol{\pi}}$ [Eq. (55)], which are

$$\delta\mathscr{L}[\Psi,\Omega,\mathbf{B},\phi] = \langle m(\mathbf{r}\cdot\partial\mathbf{J}_{r,\pi}(\mathbf{r})/\partial t)\rangle_\Omega + \oint dS(\Omega,\mathbf{r})\{(-\hbar^2/4m)\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r}) - \mathbf{r}\cdot\sigma(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})\}$$

$$+ \frac{e}{c}\oint dS(\Omega,\mathbf{r})\mathbf{r}\cdot\left[\{\mathbf{A}(\mathbf{r})\mathbf{J}(\mathbf{r}) + \mathbf{J}(\mathbf{r})\mathbf{A}(\mathbf{r})\} + \frac{e}{mc}\rho(\mathbf{r})\mathbf{A}(\mathbf{r})\mathbf{A}(\mathbf{r})\right]\cdot\mathbf{n}(\mathbf{r})$$

$$= \mathscr{V}_\pi(\Omega) - \mathscr{V}_s(\Omega) - \mathscr{V}_s^B(\Omega). \qquad (70)$$

The first term $\mathscr{V}_\pi(\Omega)$ is the virial of the force over the basin of the atom arising from a varying magnetic field. The first of the terms in the first surface integral vanishes because of the zero flux surface condition defining the atom. The second is the virial of the mechanical pressures acting on the atomic surface as determined by the stress tensor σ. The second surface integral is the virial of the magnetic pressures acting on the atomic surface. Equating the two expressions for the variation in the atomic Lagrangian given in Eqs. (69) and (70) followed by some rearrangement yields the virial theorem for an atom in a molecule in the presence of an electromagnetic field

$$-2T_\pi(\Omega) = \mathscr{V}(\Omega,\mathbf{B},\phi) = \mathscr{V}_b(\Omega) + \mathscr{V}_\phi(\Omega)$$
$$+ \mathscr{V}_B(\Omega) + \mathscr{V}_\pi(\Omega)$$
$$+ \mathscr{V}_s(\Omega) + \mathscr{V}_s^B(\Omega). \qquad (71)$$

Each of the basin and surface contributions to the atomic force [Eqs. (60) and (61)] makes a corresponding contribution to the atomic virial $\mathscr{V}(\Omega,\mathbf{B},\phi)$. As in the case of a stationary state, only the value of the total atomic virial is independent of the choice of origin for the vector $\mathbf{r}$.

The atomic statement of the virial theorem, since it defines the atomic averages of the electronic kinetic and potential energies, serves to define the electronic energy of an atom in a molecule.[1] The average electronic potential energy is equal to the virial of the forces acting over the basin of the atom. Thus the energy of an atom in a molecule in the presence of an electromagnetic field is defined to be

$$E(\Omega) = T_\pi(\Omega) + \mathscr{V}(\Omega,\mathbf{B},\phi) = -T_\pi(\Omega). \qquad (72)$$

This energy possesses the characteristic, as do all atomic properties [Eq. (1)] that it yields the average value for the total system when summed over all the atoms in the molecule

$$E = \Sigma_\Omega E(\Omega) = \langle\hat{H}\rangle, \qquad (73)$$

where the second equality assumes that no external mechanical forces act on the nuclei.

V. ATOMIC CONTRIBUTIONS TO MOLECULAR POLARIZABILITY AND SUSCEPTIBILITY

An atomic property is determined by averaging a corresponding property density over the basin of the atom.[1] The property density, however, has the essential characteristic

that it includes the effects of all the particles in the system, as determined by the property in question. This is a result of the operator being defined for the interactions experienced by a single electron and of the mode of averaging this operator over the motions of the remaining particles in the system. The density which determines the Ehrenfest force acting on the electrons provides an example of an atomic property which illustrates all of these points. The operator is $-\nabla_1 \hat{V}$, where the gradient is taken with respect to the coordinates of a single electron, and $\hat{V}$ is the many-particle potential energy operator. The operator $-\nabla_1 \hat{V}$ determines the total force exerted on the electron at r_1 by all of the other particles in the system. (It is worth noting that if one sums this operator for all of the electrons, the electron–electron contribution to the force vanishes.) The averaging of this operator over all the coordinates but $r_1 \equiv r$ by the usual recipe as determined by the atomic action principle yields the force density $F(r,t)$:

$$F(r,t) = N \int d\tau' \, \Psi^*(-\nabla_1 \hat{V}) \Psi. \qquad (74)$$

This density is N times the force exerted on the electron at r by the remaining particles in the system, the motions of the latter particles being averaged over the total system. Since the electrons are indistinguishable, multiplication by N gives the force exerted on the total density of electrons at the point r and integration of the density over the basin of the atom yields the total Ehrenfest force acting on the electrons in atom Ω. Because of the single-particle nature of the definition of a property density, the sum of the atomic contributions over the atoms in the molecule yields the molecular value for the property. It should be emphasized that the definition of an atomic property and its consequences are a result of the existence of the atomic principle of stationary action, as opposed to being the result of necessary, but otherwise arbitrarily imposed definitions.

The effect of a property density at some point in a molecule being determined by the total distribution of particles in the system is essential to the definition of atomic contributions to the electric and magnetic properties of a system. The densities for properties resulting from the molecule being placed in an external field must describe how the perturbed motion of the electron at r depends upon the field strength everywhere inside the molecule, a point that has been emphasized by others.[19–21] This requirement is met by the definition of an atomic property as determined by the theory of atoms in molecules. Property densities for a molecule in the presence of external electric and magnetic fields have been defined and discussed by Jameson and Buckingham[20] and the following discussion follows their presentation.

A. Electric polarizability

In the presence of an external field, additional terms contribute to μ, the electronic dipole moment of a molecule. These contributions may be expanded in powers of the applied field

$$\mu = \mu^{(0)} + \mu^{(1)} + \mu^{(2)} + \cdots. \qquad (75)$$

This expression may then be used to define corresponding quantities which describe the response of a system to the external field

$$\mu = \mu^{(0)} + \alpha \cdot \mathscr{E} + \tfrac{1}{2} \beta : \mathscr{E}^2 + \cdots. \qquad (76)$$

Equation (76) defines the polarizability tensor α as the quantity determining the first-order response of a molecular charge distribution to the applied field. The state function can also be expanded in terms of the field $\mathscr{E}$ to give

$$\Psi = \Psi^{(0)} + \Psi^{(1)} \mathscr{E} + \Psi^{(2)} \mathscr{E}^2 \qquad (77)$$

and, correspondingly, the charge density correct to first order in the field is given by

$$\rho(r) = N \int d\tau' \, \Psi^*\Psi = N \int d\tau' \{\Psi^{(0)*}\Psi^{(0)} + [\Psi^{(0)*}\Psi^{(1)}$$
$$+ \Psi^{(1)*}\Psi^{(0)}] \mathscr{E} + \cdots$$
$$= \rho^{(0)}(r) + \rho^{(1)}(r) \mathscr{E} + \cdots, \qquad (78)$$

where, as before, $\int d\tau'$ implies a summation over all spins and integration over all of the electronic coordinates with the exception of those denoted by the position vector r. The first-order correction to the dipole moment is related to the first-order correction to the density through the equation

$$\mu = -e \int \rho(r) r \, dr = -e \int r\rho^{(0)}(r) dr - e \int r\rho^{(1)}(r) dr \cdot \mathscr{E}, \qquad (79)$$

which, upon comparison with Eq. (76) gives

$$\mu^{(1)} = -e \int r\rho^{(1)}(r) dr \cdot \mathscr{E} = \alpha \cdot \mathscr{E}. \qquad (80)$$

One may define the electric polarizability density[20] $\alpha(r)$ as

$$\alpha(r) = -er\rho^{(1)}(r) = -eN \int d\tau' (\Psi^{(0)*} r \Psi^{(1)} + \Psi^{(1)*} r \Psi^{(0)}), \qquad (81)$$

which has the property of yielding the polarizability of the molecule when integrated over all space or the basin contribution to an atomic polarizability when integrated over the basin of an atom. Thus the basin contribution to the atomic polarizability tensor is

$$\alpha_b(\Omega) = \int_\Omega \alpha(r) dr, \qquad (82)$$

which has the property of yielding the molecular polarizability when summed over the atoms in the molecule

$$\alpha = \Sigma_\Omega \alpha_b(\Omega). \qquad (83)$$

The surface of an atom is perturbed by the applied field and the total atomic polarizability $\alpha(\Omega)$ is a sum of a basin and a surface contribution. If one denotes the basin of the atom in the field by Ω_f, the fieldfree basin by Ω_0 and the change in the basin caused the shift in the atomic surface by $\delta\Omega$, then to first order one has

$$\mu(\Omega) = -e \int_{\Omega_f} r\rho(r) dr$$
$$= -e \int_{\Omega_o} r\rho^{(0)}(r) dr - e \int_{\Omega_o} r\rho^{(1)}(r) dr \cdot \mathscr{E}$$
$$- e \int_{\delta\Omega} r\rho^{(0)}(r) dr$$
$$= \mu^{(0)}(\Omega) + \mu^{(1)}(\Omega).$$

Thus the first-order correction to the atomic electronic dipole moment is given by

$$\mu^{(1)}(\Omega) = -e\int_{\Omega_0} \mathbf{r}\rho^{(1)}(\mathbf{r})d\mathbf{r}\cdot\mathscr{E} - e\int_{\delta\Omega} \mathbf{r}\rho^{(0)}(\mathbf{r})d\mathbf{r}, \qquad (84)$$

where the final term is dependent upon the field $\mathscr{E}$ through the change in the basin resulting from the change in the atomic surface. The atomic polarizability $\alpha(\Omega)$ is therefore determined by a basin and a surface contribution

$$\alpha(\Omega) = \alpha_b(\Omega) + \alpha_s(\Omega). \qquad (85)$$

The basin contribution is given by Eq. (82) and the surface contribution by

$$\alpha_s(\Omega) = -e\int_{\delta\Omega} \mathbf{r}\rho^{(0)}(\mathbf{r})d\mathbf{r}\cdot\mathscr{E}^{-1}. \qquad (86)$$

The surface contributions cancel when summed over all the atoms in a molecule because the shifts in the interatomic surface between atoms Ω and Ω' are of opposite sign, i.e., $\delta S(\Omega,\Omega') = -\delta S(\Omega',\Omega)$ and the polarizability of the molecule is obtained by summing just the basin contributions, as given in Eq. (83). The breakdown of a perturbed atomic property into a basin and a surface contribution has been previously discussed and illustrated by Slee.[22]

To put the definition of this property into direct correspondence with the definition of other atomic properties, as one for which the property density at $\mathbf{r}$ is determined by the effect of the field over the entire molecule, we express the perturbed density in terms of the first-order corrections to the state function. This is done in a succinct manner by using the concept of a transition density.[23] The operator whose expectation value yields the total electronic charge density at the position $\mathbf{r}$ may be expressed in terms of the Dirac delta function as

$$\hat{\rho}(\mathbf{r}) = \Sigma_i\delta(\mathbf{r} - \mathbf{r}_i') = N\delta(\mathbf{r} - \mathbf{r}'). \qquad (87)$$

From the definitive property of the δ function, the zero-order contribution to the electronic dipole moment is, e.g., given by (the unperturbed state function is denoted by $|0\rangle$)

$$\mu^{(0)} = -e\int \mathbf{r}\langle 0|\hat{\rho}(\mathbf{r})|0\rangle d\mathbf{r} = -e\langle 0|\int \mathbf{r}\hat{\rho}(\mathbf{r})d\mathbf{r}|0\rangle$$

$$= -eN\langle 0|\mathbf{r}|0\rangle \qquad (88)$$

showing that the electronic density of the unperturbed state is given by

$$\rho_{00}(\mathbf{r}) = \langle 0|\hat{\rho}(\mathbf{r})|0\rangle = \rho^{(0)}(\mathbf{r}). \qquad (89)$$

The transition density $\rho_{0k}(\mathbf{r})$ is similarly defined as

$$\rho_{0k}(\mathbf{r}) = \langle 0|\hat{\rho}(\mathbf{r})|k\rangle. \qquad (90)$$

The transition density describes a charge distribution whose dipole moment is equal to the transition moment connecting states $|0\rangle$ and $|k\rangle$, the matrix element which determines the admixture of the state $|k\rangle$ to the state function for the molecule when it is perturbed by an external electric field.

The first-order correction to the charge density for a molecule in the presence of an external electric field, as defined in Eq. (78) and expressed in terms of the first-order corrections to the state function $|0\rangle$ is

$$\rho^{(1)}(\mathbf{r}) = 2\Sigma_k' \frac{\mathbf{D}_{0k}}{E_0 - E_k}\rho_{0k}(\mathbf{r}), \qquad (91)$$

where $\mathbf{D}_{0k}$ is the transition moment connecting the ground state with the excited state $|k\rangle$:

$$\mathbf{D}_{0k} = -e\int \mathbf{r}\rho_{0k}\, d\mathbf{r}. \qquad (92)$$

The first-order correction to the charge density is independent of the choice of origin for the dipole moment operator, as the extra contribuion to $\mathbf{D}_{0k}$ arising from a shift δR in origin is $-e\delta R \langle 0|k\rangle$, a term which vanishes because of the orthogonality of the zero-order states. The expression for the electric polarizability density $\alpha(\mathbf{r})$ using the above expression for the perturbed density is

$$\alpha(\mathbf{r}) = -2e\Sigma_k' \frac{\mathbf{D}_{0k}}{E_0 - E_k}\mathbf{r}\rho_{0k}(\mathbf{r}). \qquad (93)$$

One may obtain from this equation an expression for the polarization susceptibility $\alpha(\mathbf{r}',\mathbf{r}'')$:

$$\alpha(\mathbf{r}',\mathbf{r}'') = 2e^2\Sigma_k \frac{\langle 0|\mathbf{r}\delta(\mathbf{r} - \mathbf{r}'')|k\rangle\langle k|\mathbf{r}\delta(\mathbf{r} - \mathbf{r}')|0\rangle}{E_0 - E_k}. \qquad (94)$$

This expression, without the specific perturbations given by $-e\mathbf{r}$, is what Stone[21] has called the charge susceptibility of a system. It contains all of the information needed to evaluate any of the molecular polarizabilities. The polarizability density, as defined in Eq. (81), is obtained by integrating the polarization susceptibiltiy over the coordinate $\mathbf{r}''$:

$$\alpha(\mathbf{r}') = \int d\mathbf{r}''\, \alpha(\mathbf{r}',\mathbf{r}'') \qquad (95)$$

an operation in complete analogy with the procedure used to obtain the definition of the Ehrenfest force density given in Eq. (74). Thus the atomic contribution to the molecular polarizability is determined by a double integration

$$\alpha_b(\Omega) = \int_\Omega d\mathbf{r}' \int d\mathbf{r}''\, \alpha(\mathbf{r}',\mathbf{r}'') \qquad (96)$$

the first describing how the density at $\mathbf{r}'$ depends upon the effect of the field over the entire molecule, the second yielding the contribution of these effects to a particular region of space.

B. Magnetic susceptibility

A parallel development of the atomic contribution to the magnetic susceptibility of a molecule is readily obtained,[20] the charge density being replaced by the vector current density. The magnetic dipole moment $\mathbf{m}$ is defined in terms of the current density $\mathbf{J}(\mathbf{r})$ as

$$\mathbf{m} = \frac{1}{2c}\int \mathbf{r}\times\mathbf{J}(\mathbf{r})d\mathbf{r} \qquad (97)$$

and the magnetic dipole moment density $\mathbf{m}(\mathbf{r})$ is

$$\mathbf{m}(\mathbf{r}) = \frac{1}{2c}\mathbf{r}\times\mathbf{J}(\mathbf{r}). \qquad (98)$$

The expansion of the magnetic moment in powers of the applied uniform magnetic field $\mathbf{B}$ yields

$$\mathbf{m} = \mathbf{m}^{(0)} + \mathbf{m}^{(1)} + \mathbf{m}^{(2)} + \cdots = \mathbf{m}^{(0)} + \chi \cdot \mathbf{B} + \cdots , \quad (99)$$

where $\mathbf{m}^{(0)}$ is the intrinsic magnetic moment and the field-induced moment $\mathbf{m}^{(1)} = \chi \cdot \mathbf{B}$, is proportional to the magnetic susceptibility χ. Thus a magnetization density $\chi(\mathbf{r})$ can be defined as[20]

$$\chi(\mathbf{r}) \cdot \mathbf{B} = \frac{1}{2c} \mathbf{r} \times \mathbf{J}_B^{(1)}(\mathbf{r}), \quad (100)$$

where in analogy with Eq. (81) for the definition of the polarizability density in terms of the first-order density, $\mathbf{J}(\mathbf{r})_B^{(1)}$ is the first-order correction to the current density in the presence of a magnetic field. The expression for this field-induced current including the field strength $\mathbf{B}$ and the sign of the electronic charge is

$$\mathbf{J}_B^{(1)}(\mathbf{r}) = \frac{-e\hbar\mathbf{B}}{im} \int d\tau' \{\Psi^{(1)*}\nabla\Psi^{(0)} - \Psi^{(0)*}\nabla\Psi^{(1)}\}$$

$$- \frac{e^2}{mc} \mathbf{A}\rho^{(0)}(\mathbf{r}). \quad (101)$$

By using the above two equations, the magnetization density can be expressed in terms of the zero-order and first-order corrections to the state function

$$\chi(\mathbf{r}) = \frac{-e\hbar}{2imc}(\Psi^{(1)*}\mathbf{r}\times\nabla\Psi^{(0)} - \Psi^{(0)}\mathbf{r}\times\nabla\Psi^{(1)*}) - \frac{e^2}{4mc^2}$$

$$\times \rho^{(0)}(\mathbf{r})(\mathbf{r}\cdot\mathbf{r}\mathbf{I} - \mathbf{r}\mathbf{r}). \quad (102)$$

In analogy with the atomic polarizability, the atomic magnetic susceptibility consists of a basin and a surface contribution. The basin contribution to an atomic magnetic susceptibility is obtained by integrating the magnetization density over the basin of the atom

$$\chi_b(\Omega) = \int_\Omega \chi(\mathbf{r})d\mathbf{r} \quad (103)$$

and, as for the molecular polarizability, the molecular magnetic susceptibility is expressible as a sum of atomic contributions

$$\chi = \Sigma_\Omega \chi_b(\Omega). \quad (104)$$

Corresponding to Eqs. (102) and (103), one can define the atomic contributions to the magnetic shielding for a given nucleus $\sigma^N(\Omega)$ in terms of a magnetic shielding density. Jamieson and Buckingham have studied this density directly and in terms of associated difference maps for bond extension.[20]

VI. CONCLUSION

There have been many models which attempt to relate the molecular electric polarizability and magnetic susceptibility to a sum of bond or atomic contributions.[24] Certain of these models attempt to correct for the effect of the internal fields arising from the induced moments in other atoms or bonds within the molecule, one of the most successful of these being the atomic-based model proposed by Applequist[25] for the polarizability. Such problems do not of course

arise in the use of the expressions for the atomic contributions to these or related field properties using the theory of atoms in molecules, or through the use of the expression for the charge susceptibility of Stone[21] for the determination of electric polarizabilities. Stone has calculated the contributions to the polarizability of diatomic and linear triatomic molecules from regions of space defined by surfaces perpendicular to the molecular axis and midway between the nuclei or through a nucleus. Kutzelnigg[26] has proposed a coupled Hartree–Fock method with individual gauges for localized orbitals which overcomes the "gauge problem" associated with the calculation of magnetic properties and yields separate orbital contributions to both the diamagnetic and paramagnetic NMR chemical shifts. Similarly, Hansen and Bouman[27] have used localized molecular orbitals in conjunction with the random phase approximation to obtain expressions for NMR shieldings that also contain no reference to an overall gauge origin and that damp the basis set errors originating from distant groups.

The theory of atoms in molecules is being applied to a study of the atomic contributions to the polarizability, magnetic susceptibility, and nuclear magnetic shielding constants in various series of molecules.[28] These studies, in addition to accounting for the success or failure of the additivity models proposed in the past, will correlate the atomic contributions to these field-induced properties with the changes in other atomic properties, including the change in the energy of an atom in molecule as caused by the external field. An important atomic property in this regard, e.g., is the atomic average of the Fermi correlation. This quantity determines the extent to which electrons are localized within the boundaries of the atom,[29,30] a property of crucial importance to the assumptions underlying the atomic additivity schemes for field-induced properties. The theory of atoms in molecules enables one to determine the extent of transferability of field-induced atomic properties and to simultaneously obtain an understanding of the physical factors governing their values in given situations. The end result is a predictive theory of these atomic properties, based entirely upon quantum mechanics.

[1] R. F. W. Bader and T. T. Nguyen Dang, Adv. Quantum Chem. **14**, 63 (1981).
[2] S. Srebrenik and R. F. W. Bader, J. Chem. Phys. **63**, 3945 (1975); S. Srebrenik, R. F. W. Bader, and T. T. Nguyen Dang, ibid. **68**, 3667 (1978); R. F. W. Bader, S. Srebrenik, and T. T. Nguyen Dang, ibid. **68**, 3680 (1978).
[3] R. F. W. Bader, Can. J. Chem. **64**, 1036 (1986).
[4] K. Wiberg, R. F. W. Bader, and C. D. H. Lau, J. Am. Chem. Soc. **109**, 1001 (1987).
[5] R. F. W. Bader, A. Larouche, C. Gatti, M. T. Carroll, P. J. MacDougall, and K. B. Wiberg, J. Chem. Phys. **87**, 1142 (1987).
[6] J. Schwinger, Phys. Rev. **82**, 914 (1951).
[7] R. F. W. Bader, T. T. Nguyen Dang, and Y. Tal, Rep. Prog. Phys. **44**, 893 (1981).
[8] W. L Cao, C. Gatti, P. J. MacDougall, and R. F. W. Bader, Chem. Phys. Lett. **141**, 380 (1987).

[9] P. Roman, *Advanced Quantum Theory* (Addison Wesley, Reading, MA, 1965).

[10] W. Yourgrau and S. Madelstam, *Variational Principles in Dynamics and Quantum Theory* (Dover, New York, 1968).

[11] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Wiley-Interscience, New York, 1953), Vol. 1.

[12] (a) E. Schrödinger, Ann. Phys. **79**, 361 (1926); (b) **82**, 265 (1927).

[13] R. F. W. Bader, Pure Appl. Chem. **60**, 145 (1988).

[14] The other possibility, that of defining a Lagrangian integral in which each electron is assigned to a subsystem, does not lead to physically realizable boundary conditions (Ref. 2).

[15] S. T. Epstein, *The Variation Method in Quantum Chemistry* (Academic, New York, 1974), pp. 260–263. There is a plus instead of a minus sign in the magnetic force term in Eq. (8) for the Ehrenfest force. Note that this expression is for the force exerted on all the electrons and the electron–electron force is therefore, zero.

[16] R. H. Young, Mol. Phys. **16**, 509 (1969).

[17] W. Pauli, *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1958), Vol. 5, Part 1.

[18] R. F. W. Bader, J. Chem. Phys. **73**, 2871 (1980).

[19] W. J. A. Maaskant and L. J. Oosterhoff, Mol. Phys. **8**, 319 (1964).

[20] C. J. Jameson and A. D. Buckingham, J. Chem. Phys. **73**, 5684 (1980).

[21] A. J. Stone, Mol. Phys. **56**, 1065 (1985).

[22] T. S. Slee, J. Am. Chem. Soc. **108**, 7541 (1986).

[23] H. C. Longuet-Higgins, Proc. R. Soc. London Ser. A **235**, 537 (1956).

[24] P. Pascal, Ann. Chim. Phys. **19**, 5 (1910); K. G. Denbigh, Trans. Faraday Soc. **36**, 936 (1940); C. G. Le Fevre and R. J. W. Le Fevre, Rev. Pure Appl. Chem. **5**, 261 (1955).

[25] J. Applequist, Acc. Chem. Res. **10**, 79 (1977).

[26] W. Kutzelnigg, Isr. J. Chem. **19**, 193 (1980); M. Schindler and W. Kutzelnigg, J. Chem. Phys. **76**, 1919 (1982).

[27] A. E. Hansen and T. D. Bouman, J. Chem. Phys. **82**, 5035 (1985).

[28] R. F. W. Bader and K. E. Laidig (to be published).

[29] R. F. W. Bader and M. E. Stephens, J. Am. Chem. Soc. **97**, 7391 (1975).

[30] R. F. W. Bader, R. J. Gillespie, and P. J. MacDougall, J. Am. Chem. Soc. **110**, 7329 (1988).