Principle of stationary action and the definition of a proper open system

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The generalization of the variation of the action-integral operator introduced by Schwinger in the derivation of the principle of stationary action enables one to use this principle to obtain a description of the quantum mechanics of an open system. It is shown that augmenting the Lagrange-function operator by the divergence of the gradient of the density operator, a process which leaves the equations of motion unaltered, leads to a class of generators whose associated infinitesimal transformations yield variations of the action-integral operator for an open system, similar in form and content to those obtained for the total, isolated system. The augmented Lagrange-function operator and the associated action-integral operator are termed *proper* operators, since only their variation yields equations of motion for the observables of an open system, in agreement with the expressions obtained from the field equations. Modifying the generator in this manner is shown to be equivalent to requiring that the open system be bounded by a surface through which there is a local zero flux in the gradient vector field of the electron density. Only the observables of such properly defined open systems are described by the correct equations of motion. The physical significance of such proper open systems is discussed.

SCHWINGER'S PRINCIPLE AND THE DEFINITION OF AN OPEN SYSTEM

Schwinger[1] has given a formulation of quantum mechanics in which a single dynamical principle replaces the conventional array of assumptions based on the classical Hamiltonian dynamics and the correspondence principle. The principle is stated as a variational equation for the transformation function connecting eigenvectors associated with different spacelike surfaces, which describes the temporal development of the system.[1] Schwinger postulated that the generator of the infinitesimal transformation be identified with the variation of the action-integral operator, the quantity $\delta\hat{W}_{12}$, that is,

$$\delta\langle q_2,t_2|q_1,t_1\rangle=(i/\hbar)\langle q_2,t_2|\delta\hat{W}_{12}|q_1,t_1\rangle \ . \tag{1}$$

Equation (1) has been written for a particular choice of a base vector system, one which is specified by the eigenvalues, denoted by q_i, of the complete set of commuting position operators constructed from the field variables at the time t_1; that is, for a given spacelike surface. Although proposed independently by Schwinger, Eq. (1) is a translation into differential form of Feynman's path-integral formulation of quantum mechanics.[2]

The manner in which the transition amplitude is modified when infinitesimal changes occur in the dynamical variables of the quantum system can also be expressed using Dirac's transformation theory[3] in terms of the action of infinitesimal unitary generating operators, $\hat{F}(t_1)$ and $\hat{F}(t_2)$. The action of these operators on the state vectors associated with the spacelike surfaces—that is, at the two time end points—yields

$$\delta\langle q_2,t_2|q_1,t_1\rangle=(i/\hbar)\langle q_2,t_2|\hat{F}(t_2)-\hat{F}(t_1)|q_1,t_1\rangle \ . \tag{2}$$

A comparison of Eqs. (1) and (2) yields Schwinger's principle of stationary action, the operational statement of his formulation of quantum mechanics:

$$\delta\hat{W}_{12}=\hat{F}(t_2)-\hat{F}(t_1) \ . \tag{3}$$

The principle of stationary action states that changes in the action-integral operator for a given dynamical system arise only from alterations of the eigenvectors associated with the two time end points. The infinitesimal generating operators are introduced via the infinitesimal (ε) unitary operator $\hat{U}$, with $\hat{F}=\varepsilon\hat{G}$:

$$\hat{U}=\hat{1}-(i\varepsilon/\hbar)\hat{G} \ . \tag{4}$$

In this manner, Schwinger introduces Dirac's transformation theory into a generalized action principle.

Equation (3) is written for a closed isolated system, one bounded by two spacelike surfaces, but the principle applies to the general case of a system with finite spatial boundaries whose evolution with time generate a timelike surface. In this situation the change in action is generated by operators attached to both the spacelike and timelike boundary surfaces of the system, Fig. 1.

Equation (3) clearly extends the concept of stationarity of the action. Hamilton's principle[4] yields the equation of motion of the field by requiring that the action be stationary to first-order changes in the field variables, with the restrictions that the variations in the field vanish in the boundaries defining the system and that these boundaries remain fixed. The principle of stationary action, on the other hand, relaxes these restraints. It equates the variation in the action to the independent effects of changing the field components at each point in both the spacelike and timelike surfaces bounding the space-time volume defined by the action integral, and of altering the region of integration by a displacement of the points in these surfaces. Thus Eq. (3) contains the field equations, for by demanding that the change in action be dependent only on operators attached to the boundary surfaces it re-

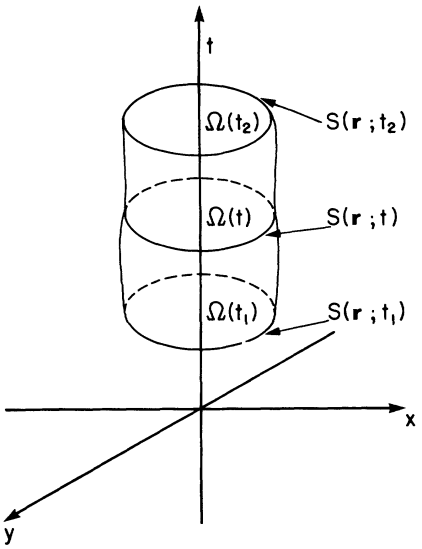

FIG. 1. Pictorial display of the space-time volume swept out by a two-dimensional open system. A spacelike surface at a given time is denoted by $\Omega(t)$, being bounded by a surface $S(\mathbf{r},t)$. The temporal evolution of the latter constitutes the timelike surface, which along with $\Omega(t_1)$ and $\Omega(t_2)$ define the space-time volume of the action integral. In the general case, the change in action is generated by operators attached to both the timelike and spacelike surfaces. However, for a proper open system, the principle of stationary action states that this change is equal to the difference in the values of the generators $\hat{F}(t)$ acting only in the two spacelike surfaces at the two time endpoints, as is the case for the total system.

quires that that variation of the action over the space-time volume bounded by these surfaces must vanish, as it does in Hamilton's principle.

The generalization of the variation of the action-integral operator to include displacements of the timelike, as well as of the spacelike, surfaces enables one to use this principle to obtain a description of the quantum mechanics of an open system. The space-time volume swept out by some total system and bounded at its two time endpoints by spacelike surfaces can be partitioned into disjoint, additive contributions by timelike surfaces, surfaces determined by the time dependence of the spatial boundaries of the constituent open systems. In addition to enabling one to determine the mechanics of an open system, one may use the principle of stationary action to inquire as to whether there is some unique prescription for defining the spatial boundaries of the open system that constitute the timelike surface.

It has been demonstrated previously[5] that the boundaries of an open system can be chosen in such a manner that the contribution resulting from the action of the generators in the timelike surface vanishes, and the principle of stationary action assumes the same form for such a subsystem as it does for the total, isolated system: that the change in action is dependent only on operators attached to the two spacelike surfaces [Eq. (3)]. The purpose of this paper is twofold: (a) to show that this choice of subsystem is equivalent to defining a particular class of infinitesimal generators; and (b) to show that only generators belonging to this class yield equations of motion for the subsystem observables that are in agreement with the expressions obtained from Schrödinger's equation or from the energy-momentum tensor for the Schrödinger field. These results suggest that the definition of an open quantum system is not open to choice, but is determined by physics.

VARIATION OF THE ACTION FOR AN OPEN SYSTEM

The action-integral operator for an open system Ω—that is, some subsystem of a total system—is the time integral of the Lagrange-function operator $\hat{\mathcal{L}}[\hat{\Psi},t,\Omega]$:

$$\hat{\mathcal{W}}_{12}[\hat{\Psi},\Omega]=\int_{t_1}^{t_2}dt\,\hat{\mathcal{L}}[\hat{\Psi},t,\Omega]$$
$$=\int_{t_1}^{t_2}dt\int_{\Omega}d\mathbf{r}\,\hat{L}(\hat{\Psi},\nabla\hat{\Psi},\dot{\hat{\Psi}})\,. \tag{5}$$

The operator $\hat{\mathcal{L}}$ is the integral of the Lagrange density operator $\hat{L}$ defined in Eq. (6) for the two-component Schrödinger field with the external potential $\hat{V}$ and the two-body interaction $g(\mathbf{r},\mathbf{r}')$:

$$\hat{L}(\hat{\Psi},\nabla\hat{\Psi},\dot{\hat{\Psi}})=\Big\{(i\hbar/2)\{\hat{\Psi}^{+}\dot{\hat{\Psi}}-\dot{\hat{\Psi}}^{+}\hat{\Psi}\}$$
$$-(\hbar^2/2m)\nabla\hat{\Psi}^{+}\cdot\nabla\hat{\Psi}-\hat{\Psi}^{+}\hat{V}\hat{\Psi}$$
$$-(\tfrac{1}{2})\int d\mathbf{r}'\hat{\Psi}^{+}(\mathbf{r})\hat{\Psi}^{+}(\mathbf{r}')g(\mathbf{r},\mathbf{r}')$$
$$\times\hat{\Psi}(\mathbf{r}')\hat{\Psi}(\mathbf{r})\Big\}\,. \tag{6}$$

Necessary summation over spin is always assumed in the integration over $\mathbf{r}$. The spatial boundary of the subsystem $S(\mathbf{r}_s,t)$, which determines the timelike surface, is a function of the time and is initially arbitrary.

According to the principle of stationary action, the variation of $\hat{\mathcal{W}}_{12}[\hat{\Psi},\Omega]$ over the space-time volume determined by the boundary of Ω must vanish and, as previously demonstrated,[6] this requirement yields Schrödinger's equation of motion for the field. The remaining contributions to $\delta\hat{\mathcal{W}}_{12}[\hat{\Psi},\Omega]$ are grouped into two sets of terms: one consisting of spatial integrals evaluated at the time endpoints, and the other consisting of time integrals evaluated at the spatial endpoints, as given in Eq. (7):

$$\delta\hat{\mathcal{W}}_{12}[\hat{\Psi},\Omega]=\left\{(i\hbar/2)\int_{\Omega}d\mathbf{r}\,\hat{\Psi}^{+}\delta\hat{\Psi}+\text{c.c.}+\int_{\Omega}d\mathbf{r}\,\hat{L}(\hat{\Psi},\nabla\hat{\Psi},\dot{\hat{\Psi}},t)\delta t\right\}\Bigg|_{t_1}^{t_2}$$
$$+\int_{t_1}^{t_2}dt\left\{(-\hbar^2/2m)\oint d\mathbf{S}(\mathbf{r}_s)\cdot(\nabla\hat{\Psi}^{+}\delta\hat{\Psi}+\text{c.c.})+\oint d\mathbf{S}(\mathbf{r}_s)\cdot\mathbf{n}\hat{L}(\hat{\Psi},\nabla\hat{\Psi},\dot{\hat{\Psi}},t)\delta S(\mathbf{r}_s)\right\}$$
$$+\int_{t_1}^{t_2}dt\left\{(-i\hbar/2)\oint d\mathbf{S}(\mathbf{r}_s)(\partial S/\partial t)\hat{\Psi}^{+}\delta\hat{\Psi}+\text{c.c.}\right\} \tag{7}$$

The first bracketed term results from the variations of the field variables in the spacelike surface (the interior of the subsystem) and from a displacement of the time, all evaluated at the two time endpoints. The second term results from variations in the timelike surfaces, being the time integral of variations of the field variables in the spatial boundary of the system and of displacements of this boundary, as denoted by $\delta S(\mathbf{r}_s)$. The final term takes explicit account of the dependence of $S(\mathbf{r}_s)$ on the time. With the exception of the final term, the definition of a generator in terms of its contributions from the spacelike and timelike surfaces given in Eq. (7) is in agreement with that determined by the generalized variation of the action given by Schwinger[1] in his Eq. (2.19). Thus his generalization of the action principle anticipates its application to an open system.

Only the contributions from the spacelike surfaces at the time endpoints survive for the total isolated system with boundaries at infinity, and in this case the expression for the change in action can be expressed as

$$\delta\hat{W}_{12}[\hat{\Psi}]=\hat{F}(t_2)-\hat{F}(t_1)$$
$$=\left\{\int d\mathbf{r}\,\hat{\Pi}\Delta\hat{\Psi}+\text{c.c.}-\int d\mathbf{r}\,\hat{H}(\hat{\Psi},\nabla^2\hat{\Psi},\dot{\hat{\Psi}})\delta t\right\}\Bigg|_{t_1}^{t_2}, \tag{8}$$

where $\hat{\Pi}=i\hbar\hat{\Psi}^{+}/2$, is the momentum conjugate to the field variable $\hat{\Psi}$, and where $\Delta\hat{\Psi}$ denotes the total variation of a field variable as given by

$$\Delta\hat{\Psi}=\delta\hat{\Psi}(\mathbf{r})+\dot{\hat{\Psi}}\delta t+\partial\hat{\Psi}\delta\mathbf{r}\ ; \tag{9}$$

that is, by a change in $\hat{\Psi}(\mathbf{r})$ at $\mathbf{r}$, and by changes resulting from spatial and temporal displacements. In analogy with the classical case, the Hamiltonian density is defined by a Lagrange transformation:

$$\hat{H}(\hat{\Psi},\nabla^2\hat{\Psi},\dot{\hat{\Psi}})=(\hat{\Pi}\dot{\hat{\Psi}}+\text{c.c.})-\hat{L}(\hat{\Psi},\nabla\hat{\Psi},\dot{\hat{\Psi}})\ . \tag{10}$$

Equation (8) identifies $-\hat{H}[\hat{\Psi}]\delta t$ with the generator of a temporal change. All other possible changes in the dynamical variables of the system are described by the generator of spatial change $\hat{\Pi}\Delta\hat{\Psi}$, the quantum analog of the classical generator $p\delta q$.[7] It is this generator that yields a derivation of the commutation relations.[1,7] The properties of interest for a subsystem are obtained through spatial variations, the time dependence of a subsystem property being obtained either from the field equation or from the principle of stationary action obtained when δt is set equal to zero, the procedure followed in the remainder of the derivation.

The field theoretic expression for a subsystem generator, using Eq. (4), is

$$\hat{F}[t,\Omega]=\int_{\Omega}d\mathbf{r}\{\hat{\Pi}\delta\hat{\Psi}(\mathbf{r})+\text{c.c.}\}$$
$$=(\varepsilon/2)\int_{\Omega}d\mathbf{r}\{\hat{\Psi}^{+}(\hat{G}\hat{\Psi})+\text{c.c.}\}\ , \tag{11}$$

which yields the following expression for the variation in the action when substituted into Eq. (7):

$$\delta\hat{\mathcal{W}}_{12}[\hat{\Psi},\Omega]=\hat{F}[t_2,\Omega]-\hat{F}[t_1,\Omega]$$
$$+\int_{t_1}^{t_2}dt\oint d\mathbf{S}(\mathbf{r}_s)\cdot\{(-\hbar^2/2m)(\nabla\hat{\Psi}^{+}\delta\hat{\Psi}+\text{c.c.})$$
$$+\mathbf{n}\hat{L}(\hat{\Psi},\nabla\hat{\Psi},\dot{\hat{\Psi}})\delta S(\mathbf{r}_s)-(i\hbar/2)(\partial S/\partial t)\hat{\Psi}^{+}\delta\hat{\Psi}+\text{c.c.}\}\ . \tag{12}$$

This result is transformed using Eq. (13), the Heisenberg equation of motion for a subsystem generator obtained from the field equation

$$d\hat{F}[t,\Omega]/dt=(\varepsilon/2)\{(i/\hbar)\langle\hat{\Psi}|[\hat{H},\hat{G}]|\hat{\Psi}\rangle_{\Omega}+\text{c.c.}\}+(\varepsilon/2)\oint d\mathbf{S}(\mathbf{r}_s)\cdot(\{(\partial S/\partial t)\hat{\Psi}^{+}\hat{G}\hat{\Psi}+\text{c.c.}\}-\{\mathbf{J}_{\hat{G}}(\mathbf{r})+\text{c.c.}\})\ . \tag{13}$$

In addition to the contribution from the interior of the subsystem as given by the commutator average in Eq. (13), there are surface contributions to the time derivative arising from the change in the surface with time and from the flux through the surface of the vector current density for the observable $\hat{G}(\mathbf{r})$, where

$$\mathbf{J}_{\hat{G}}(\mathbf{r})=(\hbar/2mi)\{\hat{\Psi}^{+}\nabla(\hat{G}\hat{\Psi})-\nabla\Psi^{+}\hat{G}\hat{\Psi}\}\ . \tag{14}$$

Use of Eq. (13) in Eq. (12), yields the following expression for the change in action for an open system with arbitrary boundaries:

$$\delta\hat{\mathcal{W}}_{12}[\hat{\Psi},\Omega]=(\varepsilon/2)\int_{t_1}^{t_2}dt\{(i/\hbar)\langle\hat{\Psi}|[\hat{H},\hat{G}]|\hat{\Psi}\rangle_\Omega+\text{c.c.}\}$$
$$+\int_{t_1}^{t_2}dt\left\{-(\hbar^2/4m)\oint d\mathbf{S}(\mathbf{r}_s)\cdot\{(\hat{\Psi}^+\nabla(\delta\hat{\Psi})+\nabla\hat{\Psi}^+\delta\hat{\Psi})+\text{c.c.}\}+\oint d\mathbf{S}(\mathbf{r}_s)\cdot\mathbf{n}\hat{L}\delta S\right\}. \quad (15)$$

For the total system with boundaries at infinity, Eq. (15) reduces to

$$\delta\hat{\mathcal{W}}_{12}[\hat{\Psi},R^3]=(\varepsilon/2)\int_{t_1}^{t_2}dt\{(i/\hbar)\langle\hat{\Psi}|[\hat{H},\hat{G}]|\hat{\Psi}\rangle+\text{c.c.}\} \quad (16)$$

with the corresponding expression for an infinitesimal time interval being

$$\delta\hat{\mathcal{L}}[\hat{\Psi},R^3]=(\varepsilon/2)\{(i/\hbar)\langle\hat{\Psi}|[\hat{H},\hat{G}]|\hat{\Psi}\rangle+\text{c.c.}\}. \quad (17)$$

Thus the principle of stationary action may be stated in a form relating Heisenberg's equation of motion for the generator to a variation of the Lagrange-function operator. It is demonstrated next that a particular choice of generator when applied to Eq. (15) yields expressions for the variation in the action-integral and Lagrange-function operators for an open system that are the same in form and content to those given in Eqs. (16) and (17) for the total isolated system.

DEFINITION OF THE PROPER ACTION AND ITS ASSOCIATED GENERATOR

One first notes an important property of the Lagrange density that is obtained when the field equations are satisfied, namely, that it reduces to the Laplacian of the density operator:[5,8]

$$\hat{L}^0=-(\hbar^2/4m)\nabla^2(\hat{\Psi}^+\hat{\Psi})=-(\hbar^2/4m)\nabla^2\hat{\rho}(\mathbf{r}), \quad (18)$$

a property that is retained in the presence of an electromagnetic field.[9] Substitution of this result into Eq. (15), the expression for the variation of the action integral for an open system with arbitrary boundaries, yields

$$\delta\hat{\mathcal{L}}[\hat{\Psi},t,\Omega]=(\varepsilon/2)\{(i/\hbar)\langle\hat{\Psi}|[\hat{H},\hat{G}]|\hat{\Psi}\rangle_\Omega+\text{c.c.}\}$$
$$-(\hbar^2/4m)\oint d\mathbf{S}(\mathbf{r}_s)\cdot(\{(\hat{\Psi}^+\nabla(\delta\hat{\Psi})+\nabla\hat{\Psi}^+\delta\hat{\Psi})+\text{c.c.}\}+\mathbf{n}\nabla^2(\hat{\Psi}^+\hat{\Psi})\delta S), \quad (19)$$

where, for brevity, the result of the substitution has been expressed in terms of the variation in the Lagrange-function operator. One next notes that the whole of the surface contribution to the variation in Eq. (19) is equal to the variation of the subsystem integral of $\hat{L}^0$, Eq. (18), and as a consequence the variation of the Lagrange-function operator can be expressed as[5]

$$\delta\hat{\mathcal{L}}[\hat{\Psi},t,\Omega]=(\varepsilon/2)\{(i/\hbar)\langle\hat{\Psi}|[\hat{H},\hat{G}]|\hat{\Psi}\rangle_\Omega+\text{c.c.}\}$$
$$-(\hbar^2/4m)\delta\left\{\int_\Omega d\mathbf{r}\nabla^2(\hat{\Psi}^+\hat{\Psi})\right\}. \quad (20)$$

Thus, because of the property of the Lagrange density exhibited in Eq. (18), the variational expressions for an open system with arbitrary boundaries differ from the corresponding expressions for the total system given in Eqs. (16) and (17) by the variation of the subsystem integral of the Laplacian of the density operator.

Schwinger[1] points out that there is an ambiguity in the definition of the Lagrange function for a given equation of motion, in that it may be augmented by the divergence of an arbitrary vector without affecting the equation of motion, only modifying the infinitesimal generating operator associated with a given surface. Clearly, one may augment the Lagrange function and its density in Eqs. (5) and (6), with the final integral appearing in Eq. (20) to yield a function labeled $\hat{\mathcal{L}}^0[\hat{\Psi},t,\Omega]$:

$$\hat{\mathcal{L}}^0[\hat{\Psi},t,\Omega]=\hat{\mathcal{L}}[\hat{\Psi},t,\Omega]+\lambda\left\{\int_\Omega d\mathbf{r}\,\nabla^2(\hat{\Psi}^+\hat{\Psi})\right\}, \quad (21)$$

where λ is an undetermined multiplier. This function, and the corresponding definition of the action integral, labeled $\hat{\mathcal{W}}^0_{12}[\hat{\Psi},\Omega]$, will be referred to, respectively, as the *proper* Lagrange function and *proper* action integral. Since the additional term is a divergence expression, its variation contributes only to the surface terms, and the field equations are again obtained. It follows from Eq. (20) that if one sets the constant λ equal to $(\hbar^2/4m)$, all contributions to the variation of the proper functionals arising from the variation of the timelike surface and its displacement vanish, with the result that that expressions for $\delta\hat{\mathcal{L}}^0[\hat{\Psi},t,\Omega]$ and $\delta\hat{\mathcal{W}}^0_{12}[\hat{\Psi},\Omega]$ are the same in form and content to those obtained for the total isolated system given in Eqs. (16) and (17); that is,

$$\delta\hat{\mathcal{L}}^0[\hat{\Psi},t,\Omega]=(\varepsilon/2)\{(i/\hbar)\langle\hat{\Psi}|[\hat{H},\hat{G}]|\hat{\Psi}\rangle_\Omega+\text{c.c.}\} \quad (22)$$

and

$$\delta\hat{\mathcal{W}}^0_{12}[\hat{\Psi},\Omega]$$
$$=(\varepsilon/2)\int_{t_1}^{t_2}dt\{(i/\hbar)\langle\hat{\Psi}|[\hat{H},\hat{G}]|\hat{\Psi}\rangle_\Omega+\text{c.c.}\}. \quad (23)$$

It is demonstrated below that Eqs. (22) and (23) obtained by the variation of the proper functionals, and only these expressions, yield equations of motion for subsystem observables that are in agreement with expressions obtained from the field equations.

UNIQUENESS OF GENERATORS DEFINED BY VARIATION OF THE PROPER ACTION

The variational results expressed in Eqs. (22) and (23) are equivalently obtained by demanding that the open systems be chosen so that the variation in the subsystem average of the Laplacian of the density operator vanishes at every stage of the variation:

$$\delta\left\{\int_\Omega d\mathbf{r}\nabla^2(\hat{\Psi}^+\hat{\Psi})\right\}=0\ . \tag{24}$$

This same constant expressed in the Schrödinger formulation is

$$\delta\left\{\langle\Psi|\int_\Omega d\mathbf{r}\,\nabla^2(\hat{\Psi}^+\hat{\Psi})|\Psi\rangle\right\}=\delta\left\{\int_\Omega d\mathbf{r}\,\nabla^2\rho(\mathbf{r})\right\}=0\ , \tag{25}$$

where $\rho(\mathbf{r})$ is the electron density whose properties describe the distribution of the nuclear and electronic charges throughout real space. The satisfaction of the variational constraint expressed in Eqs. (24) and (25) is equivalent to demanding that the subsystem be bounded by a surface exhibiting a local zero flux in the gradient vector field in the electron density,[5] as expressed in Eq. (26):

$$\langle\Psi|\nabla\hat{\rho}(\mathbf{r}_s)\cdot\mathbf{n}(\mathbf{r}_s)|\Psi\rangle=\nabla\rho(\mathbf{r}_s)\cdot\mathbf{n}(\mathbf{r}_s)=0\ ,\quad \forall\mathbf{r}\in S(\mathbf{r}_s)\ . \tag{26}$$

Thus modifying the infinitesimal generating operator by augmenting the Lagrange function in the manner described in Eq. (21) is equivalent to requiring that the open subsystem be bounded by a "zero-flux" surface in the field of $\nabla\rho(\mathbf{r})$. The application of the zero-flux boundary condition to the electron density of any system leads to its exhaustive and disjoint partitioning into regions each of which, in general, contains a single nucleus.[5,10]

Delimiting the open systems to those bounded by a zero-flux surface rids the variational expressions of the contribution arising from displacements of the surface of the open system, the term $\hat{L}\delta S$ in Eq. (15) and $\nabla^2(\hat{\Psi}^+\hat{\Psi})\delta S$ in Eq. (19), with the result that the temporal development of the associated subsystem generator is correctly governed by the flux in its vector current density. From Eqs. (13) and (19), the variation of the Lagrange function for an open system with arbitrary boundaries is given by

$$\delta\hat{\mathcal{L}}[\hat{\Psi},\Omega]=(\varepsilon/2)\int_\Omega d\mathbf{r}\,\partial\{\hat{\Psi}^+(\hat{G}\hat{\Psi})+\text{c.c.}\}/\partial t+\oint d\mathbf{S}(\mathbf{r}_s)\cdot\{(-\hbar^2/2m)(\nabla\hat{\Psi}^+\delta\hat{\Psi}+\text{c.c.}+\mathbf{n}\hat{L}^0\delta S(\mathbf{r}_s)\} \tag{27}$$

in which the term describing the explicit time dependence of the surface has been canceled out by moving the total time derivative of $\hat{F}[t,\Omega]$ within the integral. The corresponding expression for the variation of the proper Lagrange function is given in Eq. (28):

$$\delta\hat{\mathcal{L}}^0[\hat{\Psi},\Omega]=(\varepsilon/2)\int_\Omega d\mathbf{r}\,\partial\{\hat{\Psi}^+(\hat{G}\hat{\Psi})+\text{c.c.}\}/\partial t+(\varepsilon/2)\oint d\mathbf{S}(\mathbf{r}_s)\cdot(\{\mathbf{J}_G(\mathbf{r})+\text{c.c.}\})\ . \tag{28}$$

By requiring satisfaction of the variational constraint given in Eq. (24), the term involving the displacement of the surface in Eq. (27) is replaced by the surface integral of the variation of $(\hbar^2/4m)\nabla(\hat{\Psi}^+\hat{\Psi})$. The addition of this result to the remaining surface term in Eq. (27) transforms the surface contribution into one which removes from the variation the infinitesimal flux in the generator through the surface of the open system. The resulting expression is that given in Eq. (28) for a proper system. This result or the equivalent statement given in Eqs. (22) and (23) equates the variations in the proper Lagrange function and action integral to the action of generators acting solely within the interior of the open system, the essence of the principle of stationary action for a total system [Eq. (3)].

Because of the additivity of the Lagrange function and hence of the action integral, one has

$$\hat{W}_{12}[\hat{\Psi}]=\sum_\Omega\hat{W}^0_{12}[\hat{\Psi},\Omega]\ ,\quad \delta\hat{W}_{12}[\hat{\Psi}]=\sum_\Omega\delta\hat{W}^0_{12}[\hat{\Psi},\Omega]\ . \tag{29}$$

The action integral vanishes for a total system because of Eq. (18), and because of Eq. (26) it vanishes separately over each of its proper subsystems. Similarly, the total variation is the sum of contributions over the interior of each subsystem. The summations given in (29) for open systems with arbitrary boundaries would entail the cancellation of equal and oppositely directed fluxes through their common timelike surfaces. The additivity expressed in (29) applies to all properties.

PROPERTIES OF A PROPER OPEN SYSTEM

The average properties of a proper open system and their temporal behavior are determined by the variational statement of Heisenberg's equation of motion given in Eq. (22), each choice of generator yielding a corresponding subsystem theorem. Choosing $\hat{G}=\hat{\mathbf{p}}$, $\hat{\mathbf{r}}\times\hat{\mathbf{p}}$ or $\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}$, corresponding, respectively, to the generation of a rigid translation, rotation, or scaling of the coordinates of an electron over the interior of the open system, yields the force, torque, or virial theorems for an open system. These three related and important open system theorems are used to illustrate the physical consequence of using the proper Lagrange-function and action-integral operators in the definition of an open system. The discussion is given using the Schrödinger representation, the average value of a subsystem operator $\hat{G}[\Omega]$ being given by

$$\begin{aligned}G(\Omega)&=(\tfrac{1}{2})\int_\Omega d\mathbf{r}\int d\tau'[\Psi^*\hat{G}(\mathbf{r})\Psi+\text{c.c.}]\\&=(\tfrac{1}{2})\{\langle\Psi|\hat{G}[\Omega]|\Psi\rangle+\text{c.c}\}\\&=(\tfrac{1}{2})\left\{\langle\Psi|\int_\Omega\mathbf{r}\{\hat{\Psi}^+(\hat{G}\hat{\Psi})+\text{c.c.}\}|\Psi\rangle\right\},\end{aligned} \tag{30}$$

where the symbol $\int d\tau'$ denotes a summation over all spins and an integration over all spatial coordinates except those of one electron whose coordinates, denoted by $\mathbf{r}$, are integrated over the open system Ω. The resulting basic single-particle nature of the definition of the expectation value for an open system follows from the use of the corresponding generator acting on the electron with coordinate $\mathbf{r}$ in the open system variation principles.

With the infinitesimal generator $\hat{F}=\varepsilon\hat{\mathbf{p}}$, the first-order variation in $\mathcal{L}^0[\Psi,\Omega]$ is given by[5,11]

$$\delta\mathcal{L}^0[\Psi,\Omega]=\boldsymbol{\varepsilon}\cdot\nabla_{\varepsilon}\mathcal{L}^0[\Psi_{\varepsilon},\Omega]|_{\varepsilon=0}\ , \tag{31}$$

with $\Psi_{\varepsilon}(\mathbf{r},\tau',t)=\{\hat{1}-(i/\hbar)\boldsymbol{\varepsilon}\cdot\hat{\mathbf{p}}\}\Psi(\mathbf{r},\tau',t)=\Psi(\mathbf{r}-\boldsymbol{\varepsilon},\tau',t)$. Variation of the proper Lagrange integral $\mathcal{L}^0[\Psi,\Omega]$ is, by Eq. (21), equal to the sum of the variations of $\mathcal{L}[\Psi,\Omega]$ and $-L^0(\Omega)$, where

$$L^0(\Omega)=-(\hbar^2/4m)\int_{\Omega}d\mathbf{r}\,\nabla^2\rho(\mathbf{r})\ . \tag{32}$$

The variation of $\mathcal{L}[\Psi,\Omega]$, as anticipated on the basis of Eq. (27), yields

$$\boldsymbol{\varepsilon}\cdot\nabla_{\varepsilon}\mathcal{L}[\Psi_{\varepsilon},\Omega]|_{\varepsilon=0}=\boldsymbol{\varepsilon}\cdot m\int_{\Omega}d\mathbf{r}\,\partial\mathbf{J}(\mathbf{r})/\partial t-\boldsymbol{\varepsilon}\cdot(\hbar^2/4m)\oint dS\,\nabla^2\rho(\mathbf{r})\mathbf{n}(\mathbf{r})+\boldsymbol{\varepsilon}\cdot(\hbar^2/2m)\oint dS\int d\tau'\{\nabla\Psi^*\nabla\Psi+\nabla\Psi\nabla\Psi^*\}\mathbf{n}(\mathbf{r}) \tag{33}$$

which includes the contribution from the variation of the surface with $\delta S=\boldsymbol{\varepsilon}\cdot\mathbf{n}(\mathbf{r})$, and where $\mathbf{J}(\mathbf{r})$ is the vector current density, Eq. (14) with $\hat{G}=\hat{1}$. The variation of $-L^0(\Omega)$ is

$$\boldsymbol{\varepsilon}\cdot(\hbar^2/4m)\nabla_{\varepsilon}\left\{\int_{\Omega}d\mathbf{r}\nabla^2\rho_{\Psi_{\varepsilon}}\right\}=\boldsymbol{\varepsilon}\cdot(\hbar^2/4m)\oint dS\,\nabla^2\rho(\mathbf{r})\mathbf{n}(\mathbf{r})$$
$$-\boldsymbol{\varepsilon}\cdot(\hbar^2/4m)\oint dS\int d\tau'\{(\nabla\nabla\Psi^*)\Psi+\nabla\Psi^*\nabla\Psi+\nabla\Psi\nabla\Psi^*+\Psi^*\nabla\nabla\Psi\}\cdot\mathbf{n}(\mathbf{r})\ . \tag{34}$$

The addition of this result to the variation of the improper Lagrange function cancels out the surface variation and transforms the remaining surface integral into one describing the flux in the momentum density through the surface of the open system. Thus

$$\boldsymbol{\varepsilon}\cdot\nabla_{\varepsilon}\mathcal{L}^0[\Psi_{\varepsilon},\Omega]|_{\varepsilon=0}$$
$$=\boldsymbol{\varepsilon}\cdot m\int_{\Omega}d\mathbf{r}\,\partial\mathbf{J}(\mathbf{r})/\partial t-\boldsymbol{\varepsilon}\cdot\oint dS\,\boldsymbol{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})\ , \tag{35}$$

where the quantum stress tensor $\boldsymbol{\sigma}(\mathbf{r})=\mathbf{J}_{\hat{p}}(\mathbf{r})$, as introduced by Schrödinger,[12] is given by

$$\boldsymbol{\sigma}(\mathbf{r})=(\hbar^2/4m)\int d\tau'\{(\nabla\nabla\Psi^*)\Psi-\nabla\Psi^*\nabla\Psi$$
$$-\nabla\Psi\nabla\Psi^*+\Psi^*\nabla\nabla\Psi\}\ . \tag{36}$$

The stress tensor is determined by the one-electron density matrix $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$. The statement of the principle of stationary action [Eq. (22)] equates this variation in the proper Lagrange integral to the subsystem average of $[\hat{H},\hat{\mathbf{p}}]=-\nabla_r\hat{V}$, thereby yielding an expression for $\mathbf{F}(\Omega,t)$, the Ehrenfest force acting on a proper open system[11,13] (the total potential-energy operator is here denoted by $\hat{V}$):

$$\mathbf{F}(\Omega,t)=\int_{\Omega}d\mathbf{r}\int d\tau'\Psi^*(-\nabla_r\hat{V})\Psi$$
$$=m\int_{\Omega}d\mathbf{r}\,\partial\mathbf{J}(\mathbf{r})/\partial t-\oint dS\,\boldsymbol{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})\ . \tag{37}$$

This result is to be contrasted with that obtained for the variation of the Lagrange integral for an open system with arbitrary boundaries, which by Eq. (20) equates the commutator average $\mathbf{F}(\Omega,t)$ to the right-hand side of Eq. (33).

One may obtain a local expression for the Ehrenfest force, $\mathbf{F}(\mathbf{r},t)$, either by using the equations of motion to determine the time derivative $\partial\mathbf{J}(\mathbf{r})/\partial t$, as done by Pauli[14] and Epstein,[8] or by using the divergence relations satisfied by the spatial components of the energy-momentum tensor of the Schrödinger field.[13] Using again the generator for a single electron coupled with the appropriate averaging, these methods yield[5,13]

$$\mathbf{F}(\mathbf{r},t)=\int d\tau'\Psi^*(-\nabla_r\hat{V})\Psi$$
$$=m\,\partial\mathbf{J}(\mathbf{r})/\partial t-\nabla\cdot\boldsymbol{\sigma}(\mathbf{r})\ , \tag{38}$$

an expression that is, term for term, the differential form of the force given in Eq. (37) for a proper open system. The differential and integral expressions for the force acting on an open quantum system are identical in form and content to Cauchy's first law of motion in classical continuum mechanics.[15] The force density $\mathbf{F}(\mathbf{r},t)$ in Eq. (38) is the force exerted on an electron at $\mathbf{r}$ in the basin of the open system obtained by averaging the force operator $-\nabla_r\hat{V}$ over the motions of the remaining particles in the system. Its integration in Eq. (37) yields the average force exerted on the open system $\mathbf{F}(\Omega,t)$. One notes that the Ehrenfest force, even though it includes the contributions arising from the electron-electron repulsions, is totally determined by the information in the one-electron density matrix.

Proceeding in a similar manner for the generator $\hat{F}=\varepsilon\hat{\mathbf{r}}\times\hat{\mathbf{p}}$, the principle of stationary action yields the torque theorem for a proper open system:

$$\mathbf{T}(\Omega,t)=\int_{\Omega}d\mathbf{r}\int d\tau'\Psi^*(-\mathbf{r}\times\nabla_r\hat{V})\Psi$$
$$=m\int_{\Omega}d\mathbf{r}\,\mathbf{r}\times\partial\mathbf{J}(\mathbf{r})/\partial t+\oint dS\,\boldsymbol{\sigma}(\mathbf{r})\times\mathbf{r}\cdot\mathbf{n}(\mathbf{r})\ . \tag{39}$$

Taking the moment of the momentum balance given in Eq. (38) yields the differential form of this torque theorem:[16]

$$\mathbf{T}(\mathbf{r},t)=\int d\tau'\Psi^*(-\mathbf{r}\times\nabla_r\hat{V})\Psi$$
$$=m\mathbf{r}\times\partial\mathbf{J}(\mathbf{r})/\partial t+\nabla\cdot[\boldsymbol{\sigma}(\mathbf{r})\times\mathbf{r}]\ , \tag{40}$$

a result which, again, is the differential form of the corresponding theorem for a proper open system.

Finally, setting the generator $\hat{F}=\varepsilon\hat{\mathbf{r}}\cdot\hat{\mathbf{p}}$ in Eq. (22) yields the virial theorem for an open system which may be expressed as[5,11]

$$2T(\Omega)=-\int_\Omega d\mathbf{r}\int d\tau'\Psi^*(-\mathbf{r}\cdot\nabla\hat{V})\Psi$$
$$+m\int_\Omega d\mathbf{r}\,\mathbf{r}\cdot\partial\mathbf{J}(\mathbf{r})/\partial t-\oint dS\,\mathbf{r}\cdot\boldsymbol{\sigma}(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})$$
$$-(\hbar^2/4m)\oint dS\,\nabla\rho(\mathbf{r})\cdot\mathbf{n}(\mathbf{r})\ , \tag{41}$$

where the final surface contribution vanishes because of the zero-flux surface constraint on the open system. The local form of the virial theorem obtained by taking the virial of the Ehrenfest force in Eq. (38) is, term for term, the differential form of Eq. (41):[11,13]

$$2K(\mathbf{r})=-\mathbf{r}\cdot\mathbf{F}(\mathbf{r},t)+m\mathbf{r}\cdot\partial\mathbf{J}(\mathbf{r})/\partial t-\nabla\cdot[\mathbf{r}\cdot\boldsymbol{\sigma}(\mathbf{r})]$$
$$-(\hbar^2/4m)\nabla^2\rho(\mathbf{r})\ , \tag{42}$$

where $K(\mathbf{r})$ is the kinetic-energy density defined as $(-\hbar^2/4m)\int d\tau'\{\Psi^*\nabla^2\Psi+\Psi\nabla^2\Psi^*\}$ and the identity $\nabla\cdot[\mathbf{r}\cdot\boldsymbol{\sigma}(\mathbf{r})]=Tr\boldsymbol{\sigma}+\mathbf{r}\cdot\nabla\boldsymbol{\sigma}$ has been used. Because of the zero-flux surface condition defining a proper subsystem, the kinetic-energy density $K(\mathbf{r})$ integrates to the same average value $T(\Omega)$, as does the density $G(\mathbf{r})=(\hbar^2/2m)\int d\tau'\{\nabla\Psi^*\cdot\nabla\Psi\}$, since they differ locally by $-(\hbar^2/4m)\nabla^2\rho(\mathbf{r})$. For a stationary state, the local expression for the virial theorem may be stated entirely in terms of the stress tensor and its trace:[5,11]

$$-2G(\mathbf{r})=\{-\mathbf{r}\cdot\nabla\boldsymbol{\sigma}+\nabla\cdot(\mathbf{r}\cdot\boldsymbol{\sigma})\}-(\hbar^2/4m)\nabla^2\rho$$
$$=\mathcal{V}(\mathbf{r})-(\hbar^2/4m)\nabla^2\rho(\mathbf{r})\ . \tag{43}$$

The virial $\mathcal{V}(\mathbf{r})$ defined in Eq. (43) is the potential-energy density of an electron at $\mathbf{r}$. It determines the average effective potential field experienced by a single electron in a many-particle system, and provides the most short-ranged description possible of this interaction potential. This is a consequence of the electronic virial including the contribution from the nuclear-nuclear forces of repulsion $\langle\hat{V}_{nn}\rangle$ in a local manner (as the virial of the density of the Hellmann-Feynman force which the nuclei exert on the electron at $\mathbf{r}$). The average of the virial density is[5,11]

$$\mathcal{V}=\int\mathcal{V}(\mathbf{r})d\mathbf{r}=\langle\hat{V}_{ne}\rangle+\langle\hat{V}_{ee}\rangle+\langle\hat{V}_{nn}\rangle+\sum_\alpha\mathbf{X}_\alpha\cdot\nabla_\alpha E\ , \tag{44}$$

the final term being the virial of the Hellmann-Feynman forces acting on the nuclei, which vanishes in an equilibrium nuclear configuration. In interactions between systems, the repulsive potential energies $\langle\hat{V}_{ee}\rangle$ and $\langle\hat{V}_{nn}\rangle$ are each approximately one-half the magnitude of the attractive potential energy $\langle\hat{V}_{ne}\rangle$, the relatively small residual being the quantity of interest. This near cancellation is reflected in the local behavior of $\mathcal{V}(\mathbf{r})$. One may take advantage of the short-range nature of $\mathcal{V}(\mathbf{r})$ by using the local statement of the virial theorem [Eq. (43)] to define an energy density $E_e(\mathbf{r})$ as

$$E_e(\mathbf{r})=G(\mathbf{r})+\mathcal{V}(\mathbf{r})=-K(\mathbf{r})\ . \tag{45}$$

Each of the above quantities is defined in terms of the stress tensor $\boldsymbol{\sigma}(\mathbf{r})$, which in turn is determined by $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$, whose diagonal elements are the electron density $\rho(\mathbf{r})$. Each of these quantities is observed to be as locally transferable, as is $\rho(\mathbf{r})$ for a given open system in different environments. Thus the integral of $E_e(\mathbf{r})$ over a properly bounded open system yields a contribution to the total energy which parallels the transferability of the form of the open system in real space. Only an energy density defined in this manner possesses this essential physical property. All proper open systems are in general transferable to some extent, this observed property underlying the usefulness of the atomic model in chemistry.

The three theorems illustrate a general result: only the variation of the proper Lagrange function in the principle of stationary action yields theorems for an open system that are in agreement with the corresponding local expressions obtained from Schrödinger's equation. The proper integrated equation of motion for a subsystem observable contains as its sole surface term the flux in its current density through the surface of the open system, the same surface flux that appears as a divergence of the current density in the differential form of the theorem derived from Schrödinger's equation

DISCUSSION

Proper open systems, those satisfying the zero-flux surface condition, have a number of unique and important physical characteristics. Their properties, including the energy and those induced by an externally applied field, are additive to yield the corresponding expectation values for the total system. Proper open systems are the most transferable pieces one can define in an exhaustive partitioning of the real space of any system leading to their most important property; if the distribution of electronic charge is essentially unchanged for a given subsystem in two different total systems, then its properties are transferable as well as additive, the subsystem contributing the same amounts to all properties in both systems.[19] Such behavior is observed experimentally for atoms and groupings of atoms in homologous series of molecules, and gives rise to what are termed additivity schemes. The proper open systems recover the experimentally measurable additive atomic contributions to the volume, heat of formation, polarizability, and magnetic susceptibly,[5,17,18] and as a consequence they have been identified with the chemical atom. The extent of near-perfect transferability, both experimentally and theoretically, can be striking. These characteristics are a consequence of $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$, which determines all mechanical properties of a proper open system, being a short-ranged function.

The zero-flux boundary condition not only defines an atom or a grouping of atoms within a molecule, but also generalizes the idea of a Wigner-Seitz cell in a crystal by identifying it with the smallest connected region of space bounded by a zero-flux surface and exhibiting the translational invariance of the crystal.[20,21] The zero-flux boundary condition enables one to go beyond the condition of translational invariance to define and differentiate between an adsorbed atom and the adsorbing surface, between an atom in the bulk and one in the surface, or between a defect atom and its host. In every situation, one obtains a complete description of all observable properties of the crystal in terms of their atomic contributions.

The gradient vector field of ρ, in addition to determining the boundary condition for a proper open system, also determines the interatomic connectivity, the network of bonds in a molecule or a crystal yielding a theory of molecular structure and structural stability.[5,10] This topological aspect of the theory has received widespread use, including applications to the solid state, where it has been used to relate the topology of the electron density to the structure and the bulk mechanical properties of metals[22] and alloys[23] and to the diffusivity of oxygen atoms in alloys.[24]

There is much current interest in the use of local and regional relationships in the study of the solid state. Local expressions for stress and force theorems have been given by Nielsen and Martin,[25] who define a stress density for the discussion of the elastic properties of crystals. Chetty and Martin,[26] using similar concepts, define an energy density for use in the discussion of the separate contribution to the energy of a solid arising from the surface or from the presence of an impurity. Zeische and coworkers have derived expressions for energy densities and a local stress tensor in terms of one- and two-particle density matrices for the study of clusters and solids.[27,28] All three approaches make use of the local-density approximation to obtain working expressions. A comparison of these approaches with the present results goes beyond the present paper, but it is possible to note the manner in which they complement one another. First, Nielsen and Martin[25] and Chetty and Martin[26] comment on their lack of unique definitions together with the associated problems of determining regions for which one obtains results that are gauge invariant and which reflect the physical property of interest, such as that of a surface energy. All theorems that are derived here and the physical quantities they relate are uniquely defined and are obtained from a variational principle that applies to specific well-defined regions of space. These authors comment on the long-range nature of the interactions that are associated with the separate contributions to their local expressions for the energy. The subsystem energy and energy density obtained from the virial theorem for a proper open system and expressed in terms of the tensor $\sigma(\mathbf{r})$ overcome this difficulty by making use of the short rangedness of $\Gamma^{(1)}(\mathbf{r},\mathbf{r}')$. It is the demonstrated[5,17,18,29] consequence of this property of the one-density matrix that is responsible for the primary operational concept of chemistry, that of a functional group with characteristic properties. It is this energy that exhibits the essential physical requirement that two identical pieces of matter possess identical energies, be they of macroscopic dimensions or microscopic, in the form of equivalent atoms at different sites within a single crystal or two identical peptide units in a protein chain.[30]

Artacho and Falicov[31] have proposed a method for the treatment of a fermionic open system without a prescribed physical boundary, the partitioning into the open system of interest and reservoir being achieved through a corresponding partitioning of the field-theoretic Hamiltonian, together with an interaction term. The latter term explicitly includes the dynamics of the exchange of fermions between system and reservoir. While the variational principles for the proper open system presented here are of a formal nature, they do establish the existence of a unique spatial partitioning of some total system into subsystems, whose properties, in addition to being governed by quantum mechanics, are additive and reflect the characteristics of transferability associated with the working concept of an atom in a molecule or a crystal. Because the properties of proper open systems parallel the atomic model of matter, they could represent the optimum choice in the development of a general variational treatment of open systems.

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