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Time-dependent extension of the Hohenberg-Kohn-Levy energy-density functional

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An energy-minimization principle based on the hydrodynamic formulation of quantum mechanics is used to develop a time-dependent energy-density functional. The external potential considered has a periodic dependence on time and the validity of the functional is restricted to those frequencies which are not so large as to cause a transition to an excited state. The present time-dependent energy-density functional reduces to the time-independent Hohenberg-Kohn-Levy functional in the static limit.

I. INTRODUCTION

Density-functional theory for a time-independent external potential has proven to be a viable alternative to wave-function theory by Hohenberg and Kohn,[1] and Levy.[2] However, before density-functional theory can be completely accepted as a substitute for wave-function theory, an energy-density functional with a time-dependent external potential must be developed. Functionals of a time-dependent density have been given in the literature.[3,4] However, these functionals are not based on an energy-wave-function-minimization principle. For a review of these functionals as well as time-independent density functionals, see the recent article by Rajagopal.[5]

Restricting the external potential to be a real scalar potential with a periodic dependence on time, we develop an energy-wave-function-minimization principle based on the hydrodynamic-wave-function functional.[6] With this minimization principle we then construct a time-dependent energy-density functional. Our development parallels Levy's[2] recent reformulation of the Hohenberg-Kohn[1] theory, in which he solved the $\hat{v}$-representability problem and defined formally, the universal functional of the density for the sum of the kinetic and electron-electron repulsion energies. Unlike time-independent wave-function theory, the hydrodynamic-energy wave-function functional is a functional of both the amplitude and the phase of the total time-dependent wave function. Our theory provides only a method of going from a functional of the time-dependent amplitude to a functional of the time-dependent density; the functional dependence on the phase remains unchanged.

II. MINIMIZATION PRINCIPLE

Our derivation of an energy-minimization principle is based on the hydrodynamic variational principle[6]

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$$\delta J[\psi,S]-\frac{\partial}{\partial t}\langle\psi\,|\,\delta S\,|\,\psi\rangle=0\ , \tag{1}$$

and the hydrodynamic functional

$$J[\psi,S]=\left\langle\psi\left|\hat{T}+\hat{V}_{ee}+\hat{V}+\frac{\partial}{\partial t}S\right|\psi\right\rangle . \tag{2}$$

The operators in Eq. (2) are defined as

$$\hat{T}=-\tfrac{1}{2}\nabla^2+\tfrac{1}{2}(\vec{\nabla}S\cdot\vec{\nabla}S)\ , \tag{3}$$

$$\hat{V}_{ee}=\frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i-\vec{r}_j|}\ , \tag{4}$$

and $\hat{V}(\vec{r},t)$ is an adiabatically switched on time-dependent real scalar potential. (Our notations for the N-particle differential operators are $\nabla^2 f=\sum_{i=1}^{N}\nabla_i^2 f$ and $\vec{\nabla}f\cdot\vec{\nabla}g=\sum_{i=1}^{N}\vec{\nabla}_i f\cdot\vec{\nabla}_i g$, where f and g are arbitrary N-particle functions. All equations are in atomic units.) The bracket notation implies an integration over the space and spin coordinates, but not over the time coordinate. The hydrodynamic variational principle is derived from the Frenkel variational principle[7,8] by factoring the complex time-dependent wave function in terms of its modulus and argument, i.e.,

$$\Psi(\vec{r},t)=\psi(\vec{r},t)e^{iS(\vec{r},t)}\ . \tag{5}$$

Although the spin coordinates are not explicitly shown, they are contained in the amplitude $\psi(\vec{r},t)$. The electronic energy of the system of interest is defined as

$$\begin{aligned}\mathscr{E}[\Psi^*,\Psi]&=\langle\Psi|\,-\tfrac{1}{2}\nabla^2+\hat{V}_{ee}+\hat{V}\,|\Psi\rangle\\&=\langle\psi\,|\,\hat{T}+\hat{V}_{ee}+\hat{V}\,|\,\psi\rangle=\mathscr{E}[\psi,S]\ ,\end{aligned} \tag{6}$$

and is related to the hydrodynamic functional by

$$\begin{aligned}J[\Psi^*,\Psi]&=\mathscr{E}[\Psi^*,\Psi]-i\left\langle\Psi\left|\frac{\partial\Psi}{\partial t}\right.\right\rangle\\&=\mathscr{E}[\psi,S]+\left\langle\psi\left|\frac{\partial S}{\partial t}\right|\psi\right\rangle=J[\psi,S]\ .\end{aligned} \tag{7}$$

Taking independent variations with respect to ψ and S, the stationary condition, Eq. (1), yields the following set of coupled nonlinear differential equations:

$$(\hat{T}+\hat{V}_{ee}+\hat{V})\psi=-\frac{\partial S}{\partial t}\psi=E\psi \tag{8}$$

and

$$\frac{\partial}{\partial t}\psi\psi+\vec{\nabla}\cdot(\psi\psi\vec{\nabla}S)=0\ . \tag{9}$$

Since the flux of the probability density $\Psi^*\Psi=\psi\psi$ is defined as

$$\vec{j}(\vec{r},t)=\frac{i}{2}(\Psi\vec{\nabla}\Psi^*-\Psi^*\vec{\nabla}\Psi)=\psi\psi\vec{\nabla}S\ , \tag{10}$$

the equation of continuity, Eq. (9), can be written in the more familiar form

$$\frac{\partial\psi\psi}{\partial t}+\vec{\nabla}\cdot\vec{j}=0\ . \tag{11}$$

Equations (8) and (9) represent the hydrodynamic formulation of quantum mechanics. See, for instance, the recent paper by Hirschfelder[9] and the references cited in this article.

Unfortunately we do not have a functional whose variation is zero. The second term in Eq. (1) prevents $J[\psi,S]$ from having this property. Therefore, we restrict the external potential to have a periodic dependence on time. Taking a time average of $J[\psi,S]$ over one period of time Δt gives the functional

$$\begin{aligned}J[\psi,S]_t&=\frac{1}{\Delta t}\int_t^{t+\Delta t}J[\psi,S]dt'\\&=\mathscr{E}[\psi,S]_t+\left\langle\psi\left|\frac{\partial S}{\partial t}\right|\psi\right\rangle_t\ ,\end{aligned} \tag{12}$$

and the variational principle

$$\delta J[\psi,S]_t=0\ . \tag{13}$$

The subscript t on the functional and on the ket implies that a time-averaged integration has also been performed. The Euler-Lagrange equations associated with Eq. (13) are also given by Eqs. (8) and (9).

The solution $\Psi(\vec{r},t)$ of the time-dependent Schrödinger equations with a periodic time-dependent potential is a quasiperiodic function of the time.[8,10] This means that the amplitude $\psi(\vec{r},t)$ is periodic in t, but the phase $S(\vec{r},t)$ is not a periodic function of t. Actually, the phase is a sum of two terms

$$S(\vec{r},t)=S_0(t)+S_1(\vec{r},t)\ , \tag{14}$$

the first term being nonperiodic while the second term is periodic in t. The time derivative of $S_0(t)$ is obtained as an eigenvalue of Eq. (8), while $S_1(\vec{r},t)$ is obtained from Eq. (9). The electronic energy is actually a functional of ψ and S_1 and variations with respect to the phase refer to S_1.

The electronic energy $\mathscr{E}[\psi,S]_t$ is made stationary with respect to variations of ψ subject to the following constraints:

$$\langle \psi \mid \psi \rangle_t = 1 \tag{15}$$

and

$$\frac{\partial \psi\psi}{\partial t} = -\vec{\nabla}\cdot\vec{j} \ . \tag{16}$$

This is equivalent to making the following functional stationary with respect to variations in ψ:

$$\Omega[\psi,S]_t = \mathscr{E}[\psi,S]_t - \left\langle \lambda_1^{\psi} \frac{\partial \psi\psi}{\partial t} \right\rangle_t - \eta_0^{\psi} \langle \psi \mid \psi \rangle_t \ , \tag{17}$$

where λ_1^{ψ} and η_0^{ψ} are the Lagrange multipliers introduced to ensure that the solution satisfies Eqs. (15) and (16). The Lagrange multiplier $\lambda_1^{\psi}(\vec{r},t)$ is a periodic function of t. The first constraint ensures that the solutions are normalized while the second constraint preserves the charge-current conservation and ensures that the normalization is a constant of motion.

The stationary condition $\delta\Omega[\psi,S]_t = 0$ gives the following Euler-Lagrange equation:

$$\begin{aligned}(\hat{T} + \hat{V}_{ee} + \hat{V})\psi &= -\left[\frac{\partial \lambda_1^{\psi}}{\partial t} - \eta_0^{\psi} \right] \psi \\ &= -\left[\frac{\partial \lambda_1^{\psi}}{\partial t} - \frac{\partial \lambda_0^{\psi}}{\partial t} \right] \psi = E\psi \ . \end{aligned} \tag{18}$$

The relationship between the Lagrange multipliers and the phase is obtained by comparing Eq. (18) to Eq. (8). Integrating the second term in $\Omega[\psi,S]_t$ by parts over t, we find that $\Omega[\psi,S]_t$ is equivalent to $J[\psi,S]_t$.

Making $\mathscr{E}[\psi,S]_t$ stationary with respect to variations of S subject to the constraint

$$\left\langle \psi \left| \frac{\partial S}{\partial t} \right| \psi \right\rangle_t = -\mathscr{E}_t \ , \tag{19}$$

is equivalent to making the following functional stationary with respect to variations of S:

$$\Omega[\Psi,S]_t = \mathscr{E}[\psi,S]_t - \eta_0^{s} \left\langle \psi \left| \frac{\partial S}{\partial t} \right| \psi \right\rangle_t \ , \tag{20}$$

where η_0^{S} is the Lagrange multiplier which ensures Eq. (19) is satisfied by the solution. Making $\Omega[\psi,S]_t$ stationary gives the following Euler-Lagrange equation:

$$-\vec{\nabla}\cdot(\psi\psi\vec{\nabla}S) + \eta_0^{s} \frac{\partial \psi\psi}{\partial t} = 0 \ . \tag{21}$$

Comparing this equation to Eq. (9), we find that $\eta_0^{S} = -1$. Again Eq. (20) is equivalent ot $J[\psi,S]_t$.

The analysis given above shows that making $\mathscr{E}[\psi,S]_t$ stationary with respect to variations of ψ and S subject to the constraints of Eqs. (15), (16), and (19) is equivalent to the variational principle $\delta J[\psi,S]_t = 0$. This was expected since the Frenkel variational principle ensures that its solutions satisfy the proper normalization constraints.

To prove that we have an energy-minimization principle, it is sufficient to show that the second variation of $J[\psi,S]_t$

$$\tfrac{1}{2}\delta^2 J[\psi,S]_t = \langle \delta\psi \mid \hat{T} + \hat{V}_{ee} + \hat{V} - E \mid \delta\psi \rangle_t + \tfrac{1}{2} \langle \psi \mid \vec{\nabla}\delta S \cdot \vec{\nabla}\delta S \mid \psi \rangle_t + 2\langle \psi \mid \delta S \mid \delta\psi \rangle_t + 2\langle \psi \mid \vec{\nabla}S \cdot \vec{\nabla}\delta S \mid \delta\psi \rangle_t \tag{22}$$

is positive. Clearly for the ground state, the first two terms are positive, but it is not obvious that the sum of all four terms is always positive. Actually, $\delta^2 J[\psi,S]_t$ is positive for the ground state of the system of interest only when the applied frequency is not so large as to cause a transition into an excited state. For a discussion of this limitation, see Appendix A and Ref. 8. Thus, any set of trial functions which satisfy the proper boundary conditions and normalization constraint will yield an energy greater than or equal to the ground-state value as long as the applied frequency does not cause transitions into the excited states.

Before leaving this section, we will comment briefly on the static limit of $J[\psi,S]_t$, the limit in which the time dependence of $\hat{V}(\vec{r},t)$ is turned off. Taking the static limit we find that

$$\vec{\nabla}S = \vec{0} \tag{23}$$

and

$$\lambda_1^{\psi}(\vec{r},t) = 0 \ . \tag{24}$$

Therefore, the variational principle $\delta J[\psi,S]_t = 0$

(the time-dependent minimization principle) reduces properly to the Rayleigh-Ritz variational principle. Equation (8) becomes the time-independent Schrödinger equation and Eq. (9) states the obvious; the amplitude is independent of time.

III. TIME-DEPENDENT ENERGY-DENSITY FUNCTIONAL

Our derivation of an energy-density functional with a periodic time-dependent potential is based on the proof given by Levy[2] for the time-dependent problem. Restricting the external potential $\hat{V}(\vec{r},t)$ to be a sum of single-particle potentials $\hat{v}(\vec{r}_i,t)$, we define the sum of the kinetic and electron-electron repulsion energies as a functional of the electron density ρ and the phase by

$$F[\rho,S]_t = \langle \psi^{\rho}_{\min} \mid \hat{T} + \hat{V}_{ee} \mid \psi^{\rho}_{\min} \rangle_t \,. \tag{25}$$

Given ρ and S, Eq. (25) implies that we search all ψ^{ρ} which give the fixed ρ subject to the constraints of Eqs. (15) and (16), and then select that $\psi^{\rho} = \psi^{\rho}_{\min}$ which makes the expectation value of $\hat{T} + \hat{V}_{ee}$ a minimum. This minimum expectation value defines $F[\rho,S]_t$. If S is not known and we want the S which is consistent with ρ, we use a trial S to determine $\psi^{\rho}_{\min}$. Next we search all S which satisfy the constraint of Eq. (19) and choose that S which makes the expectation value a minimum. This S is used to obtain a new $\psi^{\rho}_{\min}$. The procedure is repeated until a self-consistent solution is found. Alternatively, we can use the equation of continuity to generate a self-consistent solution for S. As in the time-independent problem, $\rho(\vec{r}_1,t)$ need not be $\hat{v}(\vec{r}_1,t)$ representable.

Analogous to the time-independent theory,[2] we prove the following two theorems.

Theorem I:

$$F[\rho,S]_t + \int \rho \hat{v}\, d\vec{\sigma} \geq \mathscr{E}[\psi_{\mathrm{gs}},S_{\mathrm{gs}}]_t \,. \tag{26}$$

Theorem II:

$$F[\rho_{\mathrm{gs}},S_{\mathrm{gs}}]_t + \int \rho_{\mathrm{gs}} \hat{v}\, d\vec{\sigma} = \mathscr{E}[\psi_{\mathrm{gs}},S_{\mathrm{gs}}]_t \,. \tag{27}$$

The subscript gs stands for the ground-state solution. To simplify notation, we have defined $d\vec{\sigma}$ as $d\vec{r}_1 dt/\Delta t$.

Proof of theorem I. The definition of $F[\rho,S]_t$ allows us to construct

$$F[\rho,S]_t + \int \rho \hat{v}\, d\vec{\sigma} = \langle \psi^{\rho}_{\min} \mid \hat{T} + \hat{V}_{ee} + \hat{V} \mid \psi^{\rho}_{\min} \rangle_t \tag{28}$$

and the minimization principle proven in the last section states

$$\langle \psi^{\rho}_{\min} \mid \hat{T} + \hat{V}_{ee} + \hat{V} \mid \psi^{\rho}_{\min} \rangle_t \geq \mathscr{E}[\psi_{\mathrm{gs}},S_{\mathrm{gs}}]_t \,. \tag{29}$$

Addition of Eqs. (28) and (29) proves theorem I.

Proof of theorem II. Since the minimization principle states

$$\mathscr{E}[\psi_{\mathrm{gs}},S_{\mathrm{gs}}]_t \leq \langle \psi^{\rho_{\mathrm{gs}}}_{\min} \mid \hat{T} + \hat{V}_{ee} + \hat{V} \mid \psi^{\rho_{\mathrm{gs}}}_{\min} \rangle_t \,, \tag{30}$$

we have the following inequality:

$$\langle \psi_{\mathrm{gs}} \mid \hat{T} + \hat{V}_{ee} \mid \psi_{\mathrm{gs}} \rangle_t \leq \langle \psi^{\rho_{\mathrm{gs}}}_{\min} \mid \hat{T} + \hat{V}_{ee} \mid \psi^{\rho_{\mathrm{gs}}}_{\min} \rangle_t \,. \tag{31}$$

However, the definition of $\psi^{\rho_{\mathrm{gs}}}_{\min}$ requires

$$\langle \psi_{\mathrm{gs}} \mid \hat{T} + \hat{V}_{ee} \mid \psi_{\mathrm{gs}} \rangle_t \geq \langle \psi^{\rho_{\mathrm{gs}}}_{\min} \mid \hat{T} + \hat{V}_{ee} \mid \psi^{\rho_{\mathrm{gs}}}_{\min} \rangle_t \,. \tag{32}$$

Equations (31) and (32) can only be simultaneously satisfied if and only if the equality holds

$$\langle \psi_{\mathrm{gs}} \mid \hat{T} + \hat{V}_{ee} \mid \psi_{\mathrm{gs}} \rangle_t = \langle \psi^{\rho_{\mathrm{gs}}}_{\min} \mid \hat{T} + \hat{V}_{ee} \mid \psi^{\rho_{\mathrm{gs}}}_{\min} \rangle_t \,. \tag{33}$$

Since the right-hand side defines $F[\rho_{\mathrm{gs}},S_{\mathrm{gs}}]_t$, we have

$$F[\rho_{\mathrm{gs}},S_{\mathrm{gs}}]_t + \int \rho_{\mathrm{gs}} \hat{v}\, d\vec{\sigma} = \mathscr{E}[\psi_{\mathrm{gs}},S_{\mathrm{gs}}]_t \,, \tag{34}$$

which completes the proof of theorem II.

We could have based theorems I and II on the weaker minimization principle $\mathscr{E}[\psi,S_{\mathrm{gs}}]_t \geq \mathscr{E}[\psi_{\mathrm{gs}},S_{\mathrm{gs}}]_t$. Although this minimization principle holds regardless of the magnitude of the applied frequency, it requires that the exact ground-state solution for the phase be known. It is for this reason that we chose to base the theorems on the stronger minimization principle discussed in the last section. For a discussion of the weak minimization principle for $J[\psi,S]_t$, see Ref. 6.

We can now proceed to minimize this time-dependent energy-density functional with respect to the density, subject to the constraints which ensure the conservation of the number of particles as we did for $\mathscr{E}[\psi,S]_t$. However, before doing so, we shall reduce the overall dimensionality of the problem. Since the phase still has a $3N$-dimensional spatial dependence, and we would like the functional dependence of the energy to be with respect to single-particle functions, we make the assumption that the phase is a sum of single-particle functions $s(\vec{r}_i,t)$. It has been shown that this is not a bad assumption, at least for the first-order corrections to ψ and S due to the perturbation of a time-varying electric field.[11]

The minimization of $\mathscr{E}[\rho,s]_t$ with respect to ρ, subject to the constraints

$$\frac{\partial\rho}{\partial t}=-\vec{\nabla}_1\cdot\vec{j}_1 \tag{35}$$

and

$$\int\rho\, d\vec{\sigma}=N\ , \tag{36}$$

is equivalent to the variational principle

$$\delta\Omega[\rho]_t=0\ , \tag{37}$$

where the functional $\Omega[\rho]_t$ is defined as

$$\Omega[\rho]_t=\mathscr{E}[\rho,s]_t-\int\lambda_1^\rho\frac{\partial\rho}{\partial t}d\vec{\sigma}-\eta_0^\rho\int\rho d\vec{\sigma}\ . \tag{38}$$

Equation (38) leads to the following Euler-Lagrange equation

$$\begin{aligned}\frac{\delta\mathscr{E}[\rho,s]_t}{\delta\rho}=\frac{\delta F[\rho,s]_t}{\delta\rho}+\vec{v}&=-\left[\frac{\partial\lambda_1^\rho}{\partial t}-\eta_0^\rho\right]\\&=-\left[\frac{\partial\lambda_1^\rho}{\partial t}+\frac{\partial\lambda_0^\rho}{\partial t}\right]=\mu\ ,\end{aligned} \tag{39}$$

where λ^ρ and η_0^ρ are the Lagrange multipliers introduced to ensure that the two constraints are satisfied by the value of ρ which makes $\mathscr{E}[\rho,s]_t$ a minimum. Also, $\lambda_1^\rho(\vec{r}_1,t)$ is a periodic function of t. The first constraint ensures that the number of particles is a constant of the motion and the second constraint fixes the number of particles. The quantity $\mu(\vec{r}_1,t)$ consists of two terms

$$\mu(\vec{r}_1,t)=\mu_0+\mu_1(\vec{r}_1,t)\ , \tag{40}$$

where the second term has a periodic dependence on t. Since $\mu(\vec{r}_1,t)$ is related to the conservation of the number of particles, we call it the local chemical potential of the system. Further support for calling μ a chemical potential can be found in this following analysis. Assuming that $\mathscr{E}[\rho,s]_t$ is a continuous function of N, we have

$$\left.\frac{\partial\mathscr{E}[\rho,s]_t}{\partial N}\right|_{\vec{v}}=\int\frac{\delta\mathscr{E}[\rho,s]_t}{\delta\rho}\left[\frac{\delta N[\rho]}{\delta\rho}\right]^{-1}d\vec{\sigma}\ , \tag{41}$$

where the inverse of $\delta N/\delta\rho$, assuming that it exists, is defined by

$$\int\frac{\delta N}{\delta\rho}\left[\frac{\delta N}{\delta\rho}\right]^{-1}d\vec{\sigma}=1\ . \tag{42}$$

Evaluating Eq. (41) for a particular number of particles ($N=Z$), we have

$$\left.\frac{\partial\mathscr{E}[\rho,s]_t}{\partial N}\right|_{\vec{v},N=Z}=\mu_0+\int\mu_1\left[\frac{\delta N}{\delta\rho}\right]^{-1}d\vec{\sigma}\ . \tag{43}$$

The following relationship between the electronic energy and the local chemical potential is obtained from Eq. (39) and the definition of $\mathscr{E}[\rho,s]_t$:

$$\mathscr{E}[\rho,s]_t=\int\rho\mu\, d\vec{\sigma}-Q[\rho,s]_t\ , \tag{44}$$

where $Q[\rho,s]_t$ is defined as

$$Q[\rho,s]_t=\int\rho\frac{\delta F[\rho,s]_t}{\delta\rho}d\vec{\sigma}-F[\rho,s]_t\ . \tag{45}$$

Equations (44) and (45) are identical in form to those obtained from time-independent density-functional theory.[12]

Minimization of $\mathscr{E}[\rho,s]_t$ with respect to s subject to the constraint

$$\int\rho\frac{\partial s}{\partial t}d\vec{\sigma}=-\mathscr{E}_t\ , \tag{46}$$

gives the equation of continuity

$$\frac{\partial\rho}{\partial t}+\vec{\nabla}_1\cdot(\rho\vec{\nabla}_1 s)=\frac{\partial\rho}{\partial t}+\vec{\nabla}_1\cdot\vec{j}_1=0\ . \tag{47}$$

Equations (39) and (47) provide a set of coupled equations whose solutions determine the electronic energy of the system.

We close this section by investigating the static limit of the present density-functional theory. In the static limit we have

$$\vec{\nabla}_1 s=\vec{0} \tag{48}$$

and

$$\mu_1(\vec{r}_1,t)=0\ . \tag{49}$$

Therefore, the correct time-independent Hohenberg-Kohn-Levy[1,2] density functional and its Euler-Lagrange equation are recovered.

IV. CONCLUSION

The advantage of the present theory over the previously defined theories of Ying[3] and Peuckert[4] is that our time-dependent energy-density functional is based on a wave-function-energy-minimization principle. To allow us to briefly compare the present functional to those of Ying[3] and Peuckert,[4] we will assume that these latter functionals contain a periodic time-dependent potential.

The stationary principle considered by Ying[3] was constructed by analogy to classical hydrodynamics. Although his energy-density functional is equivalent to our functional when we make the assumption that the phase is a sum of single-particle functions, his Euler-Lagrange equation is not identical to ours. It appears that his stationary principle does not contain the proper minimization constraints for the density. Peuckert,[4] on the other hand, uses a wave-function functional which is identical to our $J[\Psi^*,\Psi]$ to construct his density functional. However, it appears that his density functional does not explicitly contain the functional dependence of the phase of the total time-dependent wave function. After this paper was submitted for publication, we learned of some recent related research of Deb and Ghosh.[14]

Our theory is restricted to external potentials which have a periodic dependence on time, and there are unanswered questions concerning the phase. Actual implementation of this theory will require not only finding useful approximations to $F[\rho,S]_t$, but also the determination of μ for each $\vec{r}$ and t. We are continuing our investigation of these several difficult problems. We hope to employ the theory in the description of time-dependent properties of atoms and molecules, and in areas of solid-state physics and the dynamics of liquids.

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APPENDIX A

The first-order corrections to ψ and S for an atom under the influence of a time-varying electric field are obtained by making the following functional stationary[13]:

$$J_2^\omega[\psi_1^\omega,S_1^\omega]=\langle\psi_1^\omega\,|\,H_0-E_0\,|\,\psi_1^\omega\rangle+2\langle\psi_1^\omega\,|\,h_1+S_1^\omega\,|\,\psi_0\rangle+\frac{1}{2\omega^2}\langle\psi_0\,|\,\vec{\nabla}S_1^\omega\cdot\vec{\nabla}S_1^\omega\,|\,\psi_0\rangle\ . \tag{A1}$$

The first-order corrections are ψ_1^ω and S_1^ω; ψ_0 is the zero-order solution, H_0 is the unperturbed Hamiltonian, E_0 is the zero-order energy, h_1 is the dipole moment operator, and ω is the frequency of incident radiation. A time-average integration has been performed and ψ_1^ω and S_1^ω are now functions of ω.

The second variation of $J_2^\omega[\psi_1^\omega,S_1^\omega]$ is given by

$$\tfrac{1}{2}\delta^2J_2^\omega[\psi_1^\omega,S_1^\omega]=\langle\delta\psi_1^\omega\,|\,H_0-E_0\,|\,\delta\psi_1^\omega\rangle+\frac{1}{\omega^2}\langle\psi_0\delta S_1^\omega\,|\,H_0-E_0\,|\,\delta s_1^\omega\psi_0\rangle+2\langle\delta\psi_1^\omega\,|\,\delta S_1^\omega\,|\,\psi_0\rangle\ . \tag{A2}$$

The second term on the right-hand side of Eq. (A2) is obtained using the identity

$$\frac{1}{2\omega^2}\langle\psi_0\,|\,\vec{\nabla}S_1^\omega\cdot\vec{\nabla}S_1^\omega\,|\,\psi_0\rangle=\frac{1}{\omega^2}\langle\psi_0S_1^\omega\,|\,[H_0,S_1]\,|\,\psi_0\rangle=\frac{1}{\omega^2}\langle\psi_0S_1^\omega\,|\,H_0-E_0\,|\,S_1^\omega\psi_0\rangle\ . \tag{A3}$$

When E_0 is the ground-state energy of the unperturbed system and ω is real, the first two terms in $\delta^2J_2[\psi_1^\omega,S_1^\omega]$ are positive. However, it is not obvious that the sum of the three terms in Eq. (A2) is positive. Since ψ_1^ω and S_1^ω are independently varied, we can take the variation in ψ_1^ω to be

$$\delta\psi_1^\omega=\frac{1}{\beta\omega}\delta S_1^\omega\psi_0\ , \tag{A4}$$

where β is an arbitrary real constant. Using Eq. (A4), the second variation of $J_2^\omega[\psi_1^\omega,s_1^\omega]$ becomes

$$\tfrac{1}{2}\delta^2J_2^\omega[\psi_1^\omega,S_1^\omega]=(1+\beta^2)\left\langle\delta\psi_1^\omega\left|H_0-E_0+\frac{2\beta}{(1+\beta^2)}\omega\right|\delta\psi_1^\omega\right\rangle\ . \tag{A5}$$

This equation is positive when

$$\omega<-\frac{(1+\beta^2)}{2\beta}\omega_{01}\ , \tag{A6}$$

where ω_{01} is the resonance frequency. This inequality is definitely satisfied for all $\beta > 0$, therefore we need only consider those $\beta < 0$. The values of ω for which Eq. (A6) is satisfied for all $\beta < 0$ are those $\omega < \omega_{01}$. Thus we see that for the trial solutions $\tilde{\psi}_1^\omega$ and $\tilde{S}_1^\omega$, the bound

$$J_2^\omega[\tilde{\psi}_1^\omega, \tilde{S}_1^\omega] \geq J_2^\omega[\psi_1^\omega, S_1^\omega] \tag{A7}$$

will be strictly valid only for those frequencies less than the first transition frequency. For the second-order corrections to ψ and S, we find that ω must be less than one-half of the transition frequency if a similar bound is to hold. For each successive order of perturbation, the interval for which we have a bound to the ground state of the system is reduced. This result is identical to that found using alternative but equivalent functionals.[8] Bounds to $J[\psi, S]$ have been discussed in the literature[6]; however, these bounds are much weaker than the ones considered in this appendix since the previous bounds required a knowledge of either ψ or S.

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