

## Brief Reports

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### Time-dependent Kohn-Sham density-functional theory

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A time-dependent Kohn-Sham theory is presented for obtaining the time-dependent density which has a periodic dependence on time. A set of coupled single-particle equations  $-\frac{1}{2}\nabla^2\chi_i + v_{\text{eff}}\chi_i = \epsilon_i\chi_i$  and  $\partial\chi_i^2/\partial t + \nabla \cdot (\chi_i^2 \nabla S_i) = 0$  are obtained. The  $\chi_i(\vec{r}, t)$  and  $S_i(\vec{r}, t)$  are the phase and amplitude, respectively, of the time-dependent Kohn-Sham orbitals,  $v_{\text{eff}}(\vec{r}, t)$  is the time-dependent Kohn-Sham effective potential, and  $\epsilon_i(\vec{r}, t) = -\partial S_i(\vec{r}, t)/\partial t$ . The density  $\rho(\vec{r}, t)$  is equal to the sum of the squares of the  $\chi_i(\vec{r}, t)$ .

#### INTRODUCTION

The time-dependent energy-density-functional theory<sup>1,2</sup> recently given in the literature is formally attractive, but like the time-independent energy-density-functional theory it is not presently suitable for practical calculations. This occurs because the energy as a functional of the density is unknown. For the time-independent problem, Kohn-Sham<sup>3</sup> formulated a density-functional theory [local spin density (LSD)], which yields the density of the chemical system. The resulting Kohn-Sham effective potential is not exactly known, but reasonable approximations to this potential are known.<sup>4,5</sup> Following the procedure of Kohn-Sham, we develop a time-dependent density-functional theory (TDLSD) which is also suitable for actual calculations. The present paper is intended to supplement our previous work on a time-dependent density-functional theory and will also be restricted to those densities which have a periodic time dependence.

#### TIME-DEPENDENT KOHN-SHAM THEORY

The local density-functional theory as developed by Kohn-Sham<sup>3</sup> determines in principle a set of single-particle orbitals  $\phi_i(\vec{r})$  whose sum of the squares equals the exact density  $\rho(\vec{r})$  of the system of interest. The Kohn-Sham orbitals are obtained by minimizing the kinetic energy of a system of  $N$

noninteracting electrons (atomic units are used throughout this paper)

$$T_s[\{\phi_i\}] = -\frac{1}{2} \sum_{i=1}^N \langle \phi_i | \nabla^2 | \phi_i \rangle, \quad (1)$$

subject to the constraints

$$\sum_{i=1}^N |\phi_i|^2 = \rho, \quad (2)$$

and

$$\langle \phi_i | \phi_j \rangle = \delta_{ij}. \quad (3)$$

The bracket notation represents an integration over configuration space. The corresponding Euler-Lagrange equation is

$$-\frac{1}{2} \nabla^2 \phi_i + v_{\text{eff}} \phi_i = \epsilon_i \phi_i, \quad (4)$$

where  $v_{\text{eff}}(\vec{r})$  is the Kohn-Sham effective potential, the Lagrange multiplier associated with Eq. (3) and the constants  $\epsilon_i$  are the Lagrange multipliers introduced to insure that Eq. (2) is satisfied by the  $\phi_i$ .

The time-dependent problem is similar to the procedure described above for the time-independent process. We seek the time-dependent orbitals  $\phi_i(\vec{r}, t)$  which yield the density  $\rho(\vec{r}, t)$  when there is a periodic dependence upon time  $t$ . The orbitals  $\phi_i(\vec{r}, t)$  can be written in polar form

$$\phi_i(\vec{r}, t) = \chi_i(\vec{r}, t) \exp[iS_i(\vec{r}, t)], \quad (5)$$

where the amplitude  $\chi_i(\vec{r}, t)$  and phase  $S_i(\vec{r}, t)$  are

real functions of space and time. The kinetic energy of noninteracting system of  $N$  electrons can now be written

$$T_s[\{\chi_i, S_i\}]_t = -\frac{1}{2} \sum_{i=1}^N (\langle \chi_i | \nabla^2 | \chi_i \rangle_t - \langle \chi_i | \bar{\nabla} S_i \cdot \bar{\nabla} S_i | \chi_i \rangle_t), \quad (6)$$

where the subscript  $t$  denotes that a time-averaged integration over one period of time has been performed.

First we minimize  $T_s[\{\chi_i, S_i\}]_t$  with respect to the  $\chi_i(\vec{r}, t)$  subject to the constraint that the sum of the squares of the  $\chi_i(\vec{r}, t)$  give the exact density  $\rho(\vec{r}, t)$ , i.e.,

$$\sum_{i=1}^N \chi_i^2 = \rho, \quad (7)$$

and further that they satisfy conservation of the number of particle constraints

$$\langle \chi_i | \chi_j \rangle_t = \delta_{ij}, \quad (8)$$

and

$$\frac{\partial \chi_i^2}{\partial t} = -\bar{\nabla} \cdot \bar{j}. \quad (9)$$

In Eq. (9),  $\bar{j}(\vec{r}, t)$  is the single-particle current vector. The resulting Euler-Lagrange equation is

$$-\frac{1}{2} \nabla^2 \chi_i + v_{\text{eff}} \chi_i = \epsilon_i \chi_i. \quad (10)$$

Again,  $v_{\text{eff}}(\vec{r}, t)$  is the Lagrange multiplier associated with the constraint defined in Eq. (7) and the  $\epsilon_i(\vec{r}, t)$  are the Lagrange multipliers associated with the conservation of particle constraints, Eqs. (8) and (9).

The  $\epsilon_i(\vec{r}, t)$  are a sum of two terms

$$\epsilon_i(\vec{r}, t) = \epsilon_i^{(0)} + \epsilon_i^{(1)}(\vec{r}, t). \quad (11)$$

The quantity  $\epsilon_i^{(0)}$  is a result of the orthonormalization constraint while  $\epsilon_i^{(1)}(\vec{r}, t)$  are the Lagrange multipliers associated with the charge-current conservation defined by Eq. (9). Next, we minimize  $T_s[\{\chi_i, S_i\}]$

with respect to the  $S_i$  subject to the constraint

$$\frac{\partial S_i}{\partial t} = -\epsilon_i. \quad (12)$$

The resulting Euler-Lagrange equation is given by

$$\frac{\partial \chi_i^2}{\partial t} + \bar{\nabla} \cdot (\chi_i^2 \bar{\nabla} S_i) = 0. \quad (13)$$

The coupled equations [Eqs. (10) and (13)] provide a means of determining the exact time-dependent density of the system of interest. We note that at the solution point the current vector is given by  $\bar{j}(\vec{r}, t) = \chi_i^2(\vec{r}, t) \bar{\nabla} S_i(\vec{r}, t)$ .

In the limit that the time dependence is turned off, TDLSD theory correctly reduces to LSD theory. In this limit  $\bar{\nabla} S_i(\vec{r}, t)$  vanishes, thus Eqs. (9), (12), and (13) are identically satisfied and Eq. (6) reduces to Eq. (1).

As with time-independent Kohn-Sham theory,  $v_{\text{eff}}(\vec{r}, t)$  is an unknown quantity. However, this should not prevent us from using TDLSD theory in performing actual calculations. Adopting the approximation of the effective potential in LSD theory (the exchange-correlation correction plus the classical electrostatic potential)<sup>4,5</sup> and adding to it the appropriate time-dependent part (say the potential due to a time-varying electric field),  $v_{\text{eff}}^{\text{approx}}$  should provide a reasonable approximation to use in Eq. (10). This construction of  $v_{\text{eff}}^{\text{approx}}$  not only introduces an error found in the LSD approximation, but also introduces an error by neglecting a contribution to  $v_{\text{eff}}$  from the many-particle phase of the total time-dependent wave function. However, we believe that this latter contribution is small<sup>6</sup> even when compared to the error associated with the LSD exchange-correlation approximation.

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