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COMMENT

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Abstract. The density functional formalism of Hohenberg, Kohn and Sham can be applied only to the calculation of the ground-state properties of the system. In general, the energy of the electronic excitations can be obtained from the self-energy operator $\Sigma(r, r', \omega)$, which requires a much larger computational effort. Recently, Fritsche has proposed a generalization of the density functional theory to excited states, that has been applied to the calculation of the band gaps of solid rare gases, alkali halides, diamond and silicon. We show that Fritsche's theory is incorrect since it is in strong disagreement with the Kohn–Sham theory when the ground state properties are considered.

Much progress has been made in recent years in the calculation of structural and electronic properties of solids from first principles. This progress has been made possible by density functional theory [1, 2] in which the massive problem of calculating the ground state of the true system of interacting electrons is rigorously transformed into that of finding the ground state of a much simpler system of non-interacting electrons moving in an effective local potential. In general, the energy of the electronic excitations can be obtained from the self-energy operator $\Sigma(r, r', \omega)$ which requires a much larger computational effort. An alternative approach has been proposed by Fritsche [3], which is based on a generalization of the density functional theory to the excited states of the system. Within such an approach, the energy of the electronic excitations in insulators and semiconductors can be expressed as a sum of the Kohn–Sham gap and a correction that is usually of the same order of magnitude. Fritsche and Gu [4] have applied the latter method to the calculation of the band gaps of solid rare gases, alkali halides, diamond and silicon, obtaining values in relatively good agreement with the GW results.

We will show that Fritsche's generalized density functional theory is incorrect since it is in strong disagreement with the Kohn–Sham theory: this result can be seen as follows.

The N-electron wavefunction Ψ_n is a solution of the Schrödinger equation

$$\mathcal{H}\Psi_n = E_n \Psi_n \tag{1}$$

where

$$\mathcal{H} = \sum_{i=1}^{N}\left[-\frac{\nabla^2}{2} + V_{ext}(r_i)\right] + \frac{1}{2}\sum_{\substack{i,j \\ i \neq j}}\frac{1}{|r_i - r_j|} \tag{2}$$

with V_{ext} and E_n denoting the external potential and the total energy of the nth excited eigenstate, respectively. The one-particle and two-particle densities are given by the following expressions

$$\rho_{n\sigma}(r) = N \int |\Psi_n(x, x_2, \ldots, x_N)|^2 \, \mathrm{d}^4 x_2 \cdots \mathrm{d}^4 x_N \tag{3}$$

$$\rho_{2,n\sigma'\sigma}(r', r) = N(N-1) \int |\Psi_n(x', x, x_3, \ldots, x_N)|^2 \, d^4x_3 \cdots d^4x_N , \quad (4)$$

where $x \equiv (r, \sigma)$ is a shorthand notation for the real space and spin coordinates, and

$$\int \ldots d^4x \equiv \sum_\sigma \int \ldots d^3r.$$

The electron–electron interaction energy $\langle V_{e-e} \rangle$ can be written as

$$\langle V_{e-e} \rangle_n = \frac{1}{2} \sum_{\sigma',\sigma} \int \int \frac{\rho_{2,n\sigma'\sigma}(r', r))}{|r' - r|} \, d^3r' \, d^3r. \quad (5)$$

If the two-particle density is partitioned as follows

$$\rho_{2,n\sigma'\sigma}(r', r) = \rho_{n\sigma'}(r')\rho_{n\sigma}(r) + \tilde{\rho}_{2,n\sigma'\sigma}(r', r) \quad (6)$$

equation (5) becomes

$$\langle V_{e-e} \rangle_n = \frac{1}{2} \sum_{\sigma',\sigma} \int \int \frac{\rho_{n\sigma'}(r')\rho_{n\sigma}(r)}{|r' - r|} \, d^3r' \, d^3r + E_{xc}^{(n)}. \quad (7)$$

Equation (7) defines the exchange–correlation energy for the nth excited eigenstate

$$E_{xc}^{(n)} = \frac{1}{2} \sum_{\sigma',\sigma} \int \int \frac{\tilde{\rho}_{2,n\sigma'\sigma}(r', r))}{|r' - r|} \, d^3r' \, d^3r. \quad (8)$$

The above definition does not coincide with the definition of the exchange–correlation energy given by Kohn and Sham [2]

$$\left\langle -\frac{\nabla^2}{2} + V_{e-e} \right\rangle = T_0[n] + \frac{1}{2} \sum_{\sigma',\sigma} \int \int \frac{\rho_{n\sigma'}(r')\rho_{n\sigma}(r)}{|r' - r|} \, d^3r' \, d^3r + E_{xc}^{KS}$$

where $T_0[n]$ is the kinetic energy of a system of non-interacting electrons, with density $n(r)$. The two expression are clearly different since it is well known that

$$T_0[n] \neq \left\langle -\frac{\nabla^2}{2} \right\rangle.$$

Fritsche [3, 5] claims that for any eigenstate Ψ_n one can uniquely construct a function $\Gamma_n^{(\sigma',\sigma)}(r'', r', r)$ with the property that

$$\delta\tilde{\rho}_{2,n\sigma'\sigma}(r'', r') = \int \Gamma_n^{(\sigma',\sigma)}(r'', r', r)\delta\rho_{n\sigma}(r) \, d^3r \quad (9)$$

where $\delta\tilde{\rho}_{2,n\sigma'\sigma}(r'', r')$ and $\delta\rho_{n\sigma}(r)$ are the changes of the two- and one-particle densities, associated with a variation of the wavefunction $\delta\Psi_n$. We point out that Fritsche has given no rigorous proof of equation (9). The change of the total electrostatic energy can be put in the following form

$$\delta\langle V \rangle_n = \sum_\sigma \int [V_{ext}(r) + V_H^{(n)}(r) + V_{xc}^{(n)}(r, \sigma)]\delta\rho_{n\sigma}(r) \, d^3r \quad (10)$$

where $V_H^{(n)}(r)$ is the Hartree potential and

$$V_{xc}^{(n)}(r, \sigma) = \frac{1}{2} \sum_{\sigma'} \int \int \frac{\Gamma_n^{(\sigma',\sigma)}(r'', r', r)}{|r'' - r'|} \, d^3r'' \, d^3r' \quad (11)$$

is the exchange–correlation potential corresponding to the *n*th excited eigenstate. From equations (8), (9) and (11) it follows that

$$\delta E_{xc}^{(n)} = \sum_\sigma \int V_{xc}^{(n)}(\boldsymbol{r}, \sigma) \delta n_\sigma(\boldsymbol{r}) \, \mathrm{d}^3 r \tag{12}$$

which is usually written

$$V_{xc}^{(n)}(\boldsymbol{r}, \sigma) = \frac{\delta E_{xc}^{(n)}}{\delta n_\sigma(\boldsymbol{r})}. \tag{13}$$

Fritsche's generalized Kohn–Sham equations are then defined as follows

$$\left[-\frac{\nabla^2}{2} + V_{ext}(\boldsymbol{r}) + V_H^{(n)}(\boldsymbol{r}) + V_{xc}^{(n)}(\boldsymbol{r}, \sigma) \right] \psi_j \sigma(\boldsymbol{r}) = \epsilon_{i\sigma}^{(n)} \psi_j \sigma(\boldsymbol{r}). \tag{14}$$

We proved above that Fritsche's exchange–correlation energy $E_{xc}^{(n)}$ is different from the Kohn–Sham exchange–correlation energy. It also follows that their functional derivatives (i.e. V_{xc}^{Frit} and V_{xc}^{K-S}) are different. In fact, one finds that

$$V_{xc}^{Frit}(\boldsymbol{r}, \sigma) = V_{xc}^{K-S}(\boldsymbol{r}, \sigma) + \frac{\delta}{\delta n_\sigma(\boldsymbol{r})} \left(T_0[n] - \left\langle -\frac{\nabla^2}{2} \right\rangle \right). \tag{15}$$

If $V_{xc}^{Frit}(\boldsymbol{r}, \sigma)$ and $V_{xc}^{K-S}(\boldsymbol{r}, \sigma)$ were coincident, it would follow that $T_0[n] - \langle -\nabla^2/2 \rangle = k$, where k is a constant independent of $n_\sigma(\boldsymbol{r})$. This is clearly false (for instance, in the case of two electrons enclosed in a potential well, the quantity $T_0[n] - \langle -\nabla^2/2 \rangle = k$ tends to zero when the dimensions of the potential well tend to infinity, which implies that k is a functional of $n_\sigma(\boldsymbol{r})$). Besides, if one supposes that $V_{xc}^{Frit}(\boldsymbol{r}, \sigma) = V_{xc}^{K-S}(\boldsymbol{r}, \sigma) + k$, where k is a constant independent of $\boldsymbol{r}$, it would follow that

$$T_0[n] - \langle -\nabla^2/2 \rangle = k \sum_\sigma \int n_\sigma(\boldsymbol{r}) \, \mathrm{d}^3 r = k Q_{tot}$$

which is again clearly false.

The exchange–correlation potential in the Kohn–Sham equations represents the correction to the external potential, necessary in order to obtain the same spin densities in the non-interacting system as in the interacting system. Since the Hohenberg–Kohn theorem prohibits two potentials from having the same ground-state density for non-interacting electrons, the exchange–correlation potential is uniquely determined by the spin densities (except for an additional constant term). It follows that the self-consistent solution of Fritsche's equations (14) gives spin densities different from those obtained from the solution of the Kohn–Sham equations. I have therefore proved that, for a given external potential $V_{ext}(\boldsymbol{r})$, Fritsche's equations (14) and the Kohn–Sham equations give different spin densities when the ground state is considered.

We conclude that Fritsche's theory is in contradiction with the Kohn–Sham theory, so that Fritsche's V_{xc}^n (which relies on the existence of the function $\Gamma_n^{(\sigma', \sigma)}$ of equation (9)) cannot exist. The present criticism applies to [3–5] since the results presented by Fritsche in such references are all based on the assumption of the existence of the function $\Gamma_n^{(\sigma', \sigma)}$.

In [4] the authors introduce integration over the coupling constant into the theory. This leads to problems in the formulation used in [3]. In fact, the coupling-constant approach would allow the definition of an exchange–correlation energy functional exactly equal to the Kohn–Sham functional, but it would also require a modification of the kinetic energy term, in order to have the same total energy functional. On the other hand, in Fritsche's theory the kinetic energy term cannot be changed, otherwise equation (14) in [10] would not be correct. Since Fritsche's derivation is based on equation (14) in [10], the whole

theory should then be proved from the beginning. We stress that the resolution of the above problems has not been explained in [4].

References

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