

Parameter-free exchange potential for excitation in the density-functional theory: Application to excitation energies within the fractional-occupation approach

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The density-functional theory for ensembles of fractional occupation formulated by Gross, Oliveira, and Kohn [Phys. Rev. A **37**, 2821 (1988)] has been applied. The excitation energies of several atoms have been determined using a parameter-free exchange potential of Gáspár [Acta Phys. Hung. **35**, 213 (1974)]. The calculated excitation energies are in good agreement with the experimental values.

I. INTRODUCTION

The density-functional theory provides a rather simple way of treating the many-electron problem. It was originally developed^{1,2} for the ground state of the electron system. Theophilou³ extended the theory to the excited states. Later Kohn⁴ investigated the density-functional theory for excited states in a quasi-local-density approximation. Gross, Oliveira, and Kohn^{5,6} formulated the density-functional theory for ensembles of unequally weighted states on the basis of the generalized Rayleigh-Ritz principle.⁷ Density-functional calculations for excited-state energies were also presented by Englisch, Fieseler, and Haufe.⁸

The density-functional theory is exact; however, the exact form of the exchange-correlation potential is not known, so approximations have to be applied. Oliveira, Gross, and Kohn⁶ calculated excitation energies of the He atom using the quasi-local-density approximation for the equiensemble exchange-correlation energy functional. Here, another approximation for the exchange potential is studied. The fractional occupation approach is applied with a parameter-free exchange potential of Gáspár.⁹ This exchange potential has proved to be suitable in calculations for the ground state of atoms and molecules.¹⁰ In this paper, it will be shown that this exchange potential can be applied to excited states as well. To test it, the first excitation energies of several atoms have been calculated and found to be in good agreement with the experimental values.

II. FRACTIONAL OCCUPATION APPROACH

Gross, Oliveira, and Kohn⁵ developed a density-functional theory for unequally weighted ensemble densities. The main results of their general formalism for the ensemble constituted by the ground state and the first excited state are as follows: One has to solve the self-consistent equations

$$\{-\Delta + \bar{v}[\rho_w](\mathbf{r})\}u_j(\mathbf{r}) = \epsilon_j u_j(\mathbf{r}), \quad (1)$$

$$\bar{v}[\rho_w](\mathbf{r}) = v(\mathbf{r}) + \int \frac{2\rho_w(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d^3r' + v_{xc}[w, \rho_w](\mathbf{r}), \quad (2)$$

where $v(r)$ is the external potential, and u_j are the one-particle orbitals. The exchange-correlation potential for the ensemble

$$v_{xc}[w, \rho](\mathbf{r}) = \frac{\delta E_{xc}[w, \rho]}{\delta \rho(\mathbf{r})} \quad (3)$$

is the functional derivative of the exchange-correlation energy functional E_{xc} and ρ_w is the weighted ensemble density. (Rydberg units are used in this paper.) ρ_w is given by

$$\rho_w(\mathbf{r}) = \frac{1-wg_2}{g_1} \sum_{m=1}^{g_1} \sum_j n_{mj} |u_j(\mathbf{r})|^2 + w \sum_{m=g_1+1}^{M_2} \sum_j n_{mj} |u_j(\mathbf{r})|^2, \quad (4)$$

where g_1 and g_2 are the degeneracy of the ground and the excited states,

$$M_2 = g_1 + g_2, \quad (5)$$

$$w = \frac{1}{M_2}, \quad (6)$$

and n_{mj} are the occupation numbers. The excitation energy takes the form

$$E_2 - E_1 = \frac{1}{g_2} \frac{d\mathcal{E}(w)}{dw}, \quad (7)$$

where the derivative of the ensemble averaged energy $\mathcal{E}(w)$ is given by

$$\frac{d\mathcal{E}(w)}{dw} = \sum_{j=N+g_1}^{N-1+M_2} \epsilon_j - \frac{g_2}{g_1} \sum_{j=N}^{N-1+g_1} \epsilon_j + \left. \frac{\partial E_{xc}[w; \rho]}{\partial w} \right|_{\rho=\rho_w}. \quad (8)$$

N is the number of electrons. The ensemble exchange-correlation potential v_{xc} and energy functional E_{xc} are different from the ground-state exchange potential and energy. Gross, Oliveira, and Kohn^{5,6} used the quasi-local-density approximation for the equiensemble exchange-correlation energy functional. Here a

parameter-free exchange potential is applied to determine the excitation energy.

III. EXCHANGE POTENTIAL

The method of providing a parameter-free local exchange potential has already been discussed in previous papers.^{9,11} Here only a summary is presented. Starting out from the free-electron-gas theory, where the exchange potential is given by

$$V_{x_1}(\mathbf{r}) = -8F(\eta) \left[\frac{3}{4\pi} \rho_{\uparrow}(\mathbf{r}) \right]^{1/3}, \quad (9)$$

$$\eta = \frac{p}{p_F}, \quad (10)$$

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right|, \quad (11)$$

an average is performed in the momentum space leading to the result

$$V_{x_1}(\mathbf{r}) = -8 \left[\frac{3}{4\pi} \rho_{\uparrow}(\mathbf{r}) \right]^{1/3} \times \left[\frac{1}{2}(\eta^3 + \eta) - \frac{1}{4}(\eta^2 - 1)^2 \ln \left| \frac{1+\eta}{1-\eta} \right| \right]_{\eta_1}^{\eta_2} \times [(\eta^3)_{\eta_1}^{\eta_2}]^{-1}. \quad (12)$$

ρ_{\uparrow} is the total electron density of the electrons with spin up and p_F is the Fermi momentum. If the average is done over the entire Fermi sphere, i.e., $\eta_1=0$ and $\eta_2=1$, the exchange potential of Slater¹² is obtained. An average carried out for a thin shell near the Fermi sphere, the thickness of which goes to zero, i.e., $\eta_1=(p_F-\epsilon)/p_F$, $\eta_2=1$ and $\epsilon \rightarrow 0$, leads to the exchange potential proposed by Gáspár¹³ and later by Kohn and Sham.² A physically more acceptable average must be between these extreme cases. So averaging near the Fermi sphere for a layer containing the reference electron, i.e., containing $v_j = u_j^* u_j$ electrons in the unit volume [$\eta_1=(1-v_j/\rho_{\uparrow})^{1/3}$ and $\eta_2=1$], the exchange potential

$$V_{x_1}^j(\mathbf{r}) = -6 \left[\frac{3}{4\pi} \rho_{\uparrow}(\mathbf{r}) \right]^{1/3} \alpha_j(\mathbf{r}) \quad (13)$$

for spin orbital u_j , where

$$\alpha_j(\mathbf{r}) = \frac{\rho_{\uparrow}}{v_j} \left[1 - \frac{1}{2}\eta_j^3 - \frac{1}{2}\eta_j + \frac{1}{4}(\eta_j^2 - 1)^2 \ln \left| \frac{1+\eta_j}{1-\eta_j} \right| \right] \quad (14)$$

and

$$\eta_j = (1 - v_j/\rho_{\uparrow})^{1/3}. \quad (15)$$

To eliminate the need for different potentials for different orbitals an average for the shells is done and the potential is given by

$$V_{x_1}(\mathbf{r}) = -6\alpha_1(\mathbf{r}) \left[\frac{3}{4\pi} \rho_{\uparrow}(\mathbf{r}) \right]^{1/3}, \quad (16)$$

where

$$\alpha_1(\mathbf{r}) = \frac{\sum_j n_j \alpha_j(\mathbf{r})}{\sum_j n_j} \quad (17)$$

and n_j is the number of the electrons in the shell j . It has been shown¹¹ that the function $\alpha(\mathbf{r})$ is very close to a constant value. As the potential (13) depends explicitly on the spin orbital considered it is very flexible and it can be successfully applied in both ground- and excited-state calculations.

IV. RESULTS AND DISCUSSION

The potential v_{xc} in Eq. (2) is approximated by the potential V_x in Eq. (16). The ground state and the ensemble potentials are different not only because the ground state and ensemble densities are different but because α in Eq. (17) has different values for the ground state and the ensemble spin orbitals. However, there is only a small difference between the ground state and the ensemble α . (It has already been shown¹¹ that α depends above all on the number of electrons.) So the explicit dependence of E_x on w is negligible and the excitation energy can be approximated by

$$E_2 - E_1 \approx \frac{1}{g_2} \sum_{j=N+g_1}^{N-1+M_2} \epsilon_j - \frac{1}{g_1} \sum_{j=N}^{N-1+g_1} \epsilon_j. \quad (18)$$

The excitation energies of certain atoms are presented

TABLE I. Excitation energies of certain atoms (in Ry).

Atom	Ground state	Excited state	Ensemble state	Calculated excitation	Experimental energy
B	$2p(^2P)$	$3s(^2S)$	$2p^{0.75}3s^{0.25}$	0.291	0.365
C	$2p^2(^3P)$	$3s(^3P)$	$2p^{1.5}3s^{0.5}$	0.523	0.550
O	$2p^4(^3P)$	$3s(^3S)$	$2p^{3.75}3s^{0.25}$	0.762	0.698
F	$2p^5(^2P)$	$3s(^2P)$	$2p^{4.5}3s^{0.5}$	1.088	0.946
Na	$3s(^2S)$	$3p(^2P)$	$3s^{0.25}3p^{0.75}$	0.151	0.154
Mg	$3s^2(^1S)$	$3p(^1P)$	$3s^{1.25}3p^{0.75}$	0.256	0.259
Al	$3p(^2P)$	$4s(^2S)$	$3p^{0.75}4s^{0.25}$	0.168	0.231
Si	$3p^2(^3P)$	$4s(^3P)$	$3p^{1.5}4s^{0.5}$	0.314	0.368
P	$3p^3(^4S)$	$4s(^4P)$	$3p^{2.25}4s^{0.75}$	0.487	0.512
Cl	$3p^5(^2P)$	$4s(^2P)$	$3p^{4.5}4s^{0.5}$	0.707	0.665

in Table I. Besides the ground-state and excited-state configurations, Table I also contains the fractional occupation configurations of the ensemble states. For comparison the experimental excitation energies¹⁴ are presented, too. There is a good agreement between the calculated and the experimental excitation energies, except in a few cases. Here the results of an exchange-only non-spin-polarized calculation are presented. Perhaps this is why there are slightly larger derivations from the

experimental data in certain cases. It is interesting to note that in several cases the fractional occupation configuration of the ensemble state is the same as the transition-state configuration of Slater.¹⁵

In conclusion, it can be stated that the parameter-free potential of Gáspár provides generally adequate results for the first excited states. It is believed that the method can also be applied for molecules.

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