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2001 J. Phys. B: At. Mol. Opt. Phys. 34 2363

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An alternative optimized potential method for ensembles of excited states

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Received 17 January 2001, in final form 29 March 2001

Abstract

Recently an optimized potential method (OPM) has been derived for ensembles of excited states. Here an alternative OPM is proposed. The ensemble Kohn–Sham potential in the generalized version of the Krieger–Li–Iafrate approximation to the OPM method is obtained.

1. Introduction

There are several ways to treat excited states in density-functional theory [1]. To calculate excitation energies Slater [2] introduced the so-called transition-state method. Density-functional theory was first rigorously generalized for excited states by Theophilou [3]. A more general treatment was given by Gross *et al* [4]. The relativistic generalization of this formalism has also been performed [5]. Recently, Görling [6] presented a new density-functional formalism for excited states generalizing recent perturbation theory [7]. Gross *et al* [4] calculated the excitation energies of the He atom using the quasi-local-density approximation of Kohn [8]. The ensemble method was applied to obtain excitation energies of several atoms [9–12] and several approximate functionals have also been tested [13]. The coordinate scaling for the density matrix of ensembles has been explored [14]. The ground-state adiabatic connection formula has been extended to the ensemble exchange–correlation energy and a simple local ensemble exchange potential has been proposed [15].

In addition to ensemble density-functional theory time-dependent density-functional theory can also be used to calculate excitation energies [16]. (For reviews of excited-state theories see [12, 17].) Recently, time-independent theories for a single excited state have also been proposed [18–20].

Unfortunately, the exchange–correlation part of the ensemble Kohn–Sham potential is not known exactly. In ground-state theory the exchange potential can be treated exactly using the optimized potential method (OPM) [21–24]. In a previous paper the optimized potential was defined for ensembles of excited states. It was based on the ensemble Hartree–Fock method [25]. Here an alternative OPM is proposed. The ensemble Kohn–Sham potential in the generalized version of the Krieger–Li–Iafrate (KLI) approximation to the OPM is obtained.

2. Density-functional theory for ensembles

First the density-functional theory for ensembles is summarized [3,4]. The eigenvalue problem of the Hamiltonian \hat{H} is given by

$$\hat{H}\Psi_k = E_k\Psi_k \quad (k = 1, \dots, M) \quad (1)$$

where

$$E_1 \leq E_2 \leq \dots \quad (2)$$

are the energy eigenvalues. The generalized Rayleigh–Ritz variational principle [4] can be applied to the ensemble energy

$$\mathcal{E} = \sum_{k=1}^M w_k E_k, \quad (3)$$

where $w_1 \geq w_2 \geq \dots \geq w_M \geq 0$. The generalized Hohenberg–Kohn theorems read as follows: (i) the external potential $v(r)$ is determined within a trivial additive constant by the ensemble density n defined as

$$n = \sum_{k=1}^M w_k n_k. \quad (4)$$

(ii) For a trial ensemble density $n'(r)$ such that

$$n'(r) \geq 0 \quad (5)$$

and

$$\int n'(r) dr = N \quad (6)$$

$$\mathcal{E}[n] \leq \mathcal{E}[n']. \quad (7)$$

The ensemble functional \mathcal{E} takes its minimum at the correct ensemble density n .

The Kohn–Sham equations for the ensemble can also be derived:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{KS}} \right] u_i(r) = \epsilon_i u_i(r). \quad (8)$$

The ensemble Kohn–Sham potential

$$v_{\text{KS}}(\mathbf{r}; w, n_w) = v(\mathbf{r}) + v_c(\mathbf{r}; w, n_w) + v_{\text{xc}}(\mathbf{r}; w, n_w), \quad (9)$$

is a sum of the external, the ensemble Coulomb and the ensemble exchange–correlation potentials.

3. Optimized potential method for ensembles of excited states

Though the Kohn–Sham approach is an exact scheme, unfortunately, the exchange–correlation part of this Kohn–Sham potential is not known exactly. In ground-state theory the exchange potential can be exactly determined by finding the optimized effective potential [21–24, 26].

The OPM can be applied when the total energy is given as a functional of the one-electron orbitals. In this case the total ensemble energy \mathcal{E} is considered as a functional of the ensemble Kohn–Sham orbitals. The energy E_k in equation (3) can be written as

$$E_k = T_k + \int n_k(\mathbf{r})v(\mathbf{r}) + E_c^k + E_{\text{xc}}^k, \quad (10)$$

where E_{xc}^k

$$E_c^k = \frac{1}{2} \int \frac{n_k(\mathbf{r})n_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (11)$$

$$n_k = \sum_j \lambda_j^k |\phi_j|^2 \quad (12)$$

and

$$T_k = -\frac{1}{2} \sum_j \lambda_j^k \int \phi_j^* \nabla^2 \phi_j d\mathbf{r} \quad (13)$$

are the exchange–correlation energy, the Coulomb energy, the density and the kinetic energy corresponding to the eigenvalue k , respectively. A different notation ϕ_j is used for the orbitals because the solutions of equation (24) are not exactly the same as the Kohn–Sham ensemble orbitals u_j . The total ensemble energy can be written as

$$\mathcal{E}[\phi_j] = T + \int n(\mathbf{r})v(\mathbf{r}) + E_c + E_{xc} \quad (14)$$

where

$$T = \sum_k w_k T_k = -\frac{1}{2} \sum_j \alpha_j \int \phi_j^* \nabla^2 \phi_j d\mathbf{r}, \quad (15)$$

$$E_c = \sum_k w_k E_c^k, \quad (16)$$

$$E_{xc} = \sum_k w_k E_{xc}^k \quad (17)$$

and

$$\alpha_j = \sum_k w_k \lambda_j^k \quad (18)$$

are the ensemble occupation numbers. The local effective optimized potential $V(\mathbf{r})$ minimizes the total ensemble energy \mathcal{E} :

$$\frac{\delta \mathcal{E}}{\delta V} = \sum_j \int \frac{\delta \mathcal{E}}{\delta \phi_j^*(\mathbf{r}')} \frac{\delta \phi_j^*(\mathbf{r}')}{\delta V(\mathbf{r})} d\mathbf{r}' + \text{c.c.} = 0. \quad (19)$$

The functional derivative of the one-electron orbitals ϕ_j with respect to the local effective potential V can be calculated with the help of the Green function

$$\frac{\delta \phi_j^*(\mathbf{r}')}{\delta V(\mathbf{r})} = -G_j(\mathbf{r}', \mathbf{r}) \phi_j(\mathbf{r}), \quad (20)$$

and an integral equation for V can be derived:

$$0 = \sum_j \alpha_j \int [V_j(\mathbf{r}') - V_c(\mathbf{r}') - V_{xc}(\mathbf{r}')] G_j(\mathbf{r}', \mathbf{r}) \phi_j^*(\mathbf{r}') \phi_j(\mathbf{r}) + \text{c.c.}, \quad (21)$$

where

$$V_j(\mathbf{r}) = \frac{1}{\alpha_j \phi_j^*(\mathbf{r})} \frac{\delta(E_c + E_{xc})}{\delta \phi_j(\mathbf{r})} \quad (22)$$

and $V(\mathbf{r})$ is written as a sum of the external, the classical Coulomb and exchange–correlation potential

$$V(\mathbf{r}) = v(\mathbf{r}) + V_c(\mathbf{r}) + V_{xc}(\mathbf{r}). \quad (23)$$

It is very difficult to calculate the effective potential V because of some vast numerical problems. So as an approximation the ensemble analogue of the KLI [24] approach is presented.

The variation of the total ensemble energy \mathcal{E} with respect to the orbitals leads to the equations

$$\left[-\frac{1}{2}\nabla^2\phi_j + (v + V_c^j + V_{xc}^j)\phi_j \right] = \varepsilon_j\phi_j, \quad (24)$$

where

$$V_c^j = \frac{\sum_k w_k \lambda_j^k v_c^k}{\sum_k w_k \lambda_j^k} \quad (25)$$

and

$$V_{xc}^j = \frac{\sum_k w_k \lambda_j^k v_{xc}^k}{\sum_k w_k \lambda_j^k} \quad (26)$$

are orbital-dependent ensemble Coulomb and exchange–correlation potentials, respectively

$$v_c^k = \int \frac{n_k(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (27)$$

and

$$v_{xc}^k = \frac{1}{\lambda_j} \frac{\delta E_{xc}^k[\phi_j]}{\delta \phi_j^*}. \quad (28)$$

Note that these ensemble Coulomb and exchange–correlation potentials are different for different orbitals.

Using the method of the author [26] new potentials (being the same for each orbital) are derived. Introducing the K_j functions as

$$\phi_j = K_j n^{1/2}, \quad (29)$$

substituting this into equation (24) and summing for all orbitals, after some algebra, we arrive at the equation

$$\left[\frac{1}{8} \left(\frac{\nabla n}{n} \right)^2 - \frac{1}{4} \frac{\nabla^2 n}{n} \right] + \frac{1}{2} \sum_j \alpha_j |\nabla K_j|^2 + v + V_S = \sum_j \alpha_j \varepsilon_j |K_j|^2, \quad (30)$$

where the Slater potential

$$V_S = V_S^c + V_S^{xc} \quad (31)$$

has both Coulomb and exchange–correlation parts

$$V_S^c = \sum_j \alpha_j |K_j|^2 V_c^j \quad (32)$$

$$V_S^{xc} = \sum_j \alpha_j K_j V_{xc}^j K_j. \quad (33)$$

From expressions (25) and (26) these potentials have the form

$$V_S^c = \sum_k w_k \frac{n_k}{n} v_c^k \quad (34)$$

$$V_S^{xc} = \sum_k w_k \frac{n_k}{n} v_{xc}^k, \quad (35)$$

that is the ensemble average of the Coulomb and exchange–correlation potentials weighted with the densities.

Introducing k_j functions with the definition

$$u_j = k_j n^{1/2} \quad (36)$$

the ensemble Kohn–Sham equations (8) can be rewritten as

$$\left[\frac{1}{8} \left(\frac{\nabla n}{n} \right)^2 - \frac{1}{4} \frac{\nabla^2 n}{n} \right] + \frac{1}{2} \sum_j \alpha_j |\nabla k_j|^2 + v_{\text{KS}} = \sum_j \alpha_j \epsilon_j |k_j|^2. \quad (37)$$

A comparison of equations (30), (37) and (9) leads to the following expression for the sum of the Coulomb and exchange–correlation potentials:

$$V_{\text{cxc}} = V_{\text{c}} + V_{\text{xc}} = V_{\text{S}} + \sum_j \alpha_j (\epsilon_j - \varepsilon_j) |k_j|^2 - \sum_j \alpha_j \varepsilon_j (|K_j|^2 - |k_j|^2) - \frac{1}{2} \sum_j \alpha_j [|\nabla k_j|^2 - |\nabla K_j|^2]. \quad (38)$$

This is an exact expression for the sum of the ensemble Coulomb and exchange–correlation potentials.

In the following the method is detailed in the exchange-only case, where the exchange energy E_k is given by

$$E_{\text{x}}^k = -\frac{1}{2} \sum_i \sum_j \lambda_i^k \lambda_j^k \int \frac{u_i^*(\mathbf{r}) u_j^*(\mathbf{r}') u_j(\mathbf{r}) u_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'. \quad (39)$$

Then the generalized ensemble KLI [24] approximation to the OPM follows with the assumption that $K_i \approx k_i$:

$$V_{\text{cx}} = V_{\text{S}} + \sum_j \alpha_j \frac{|u_j|^2}{n} \langle u_j | V_{\text{cx}} - V_{\text{cx}}^j | u_j \rangle, \quad (40)$$

where

$$V_{\text{cx}}^j = V_{\text{c}}^j + V_{\text{x}}^j \quad (41)$$

is the sum of the Coulomb and exchange potentials of orbital j .

4. Example and discussion

As an illustration the ensemble and excitation energies of the He atom were determined using the KLI approximation presented here. Following Oliveira and co-workers [4] the average energies of the singlet and triplet levels were calculated. Table 1 contains the ensemble energies. For comparison the experimental energies [28] and the values calculated by Oliveira and co-workers [4] are also shown. The latter were computed using the quasi-local-density approximation proposed by Kohn [8]. In the calculations the maximum possible values of the weighting factors are selected. The present KLI method gives much better results than the quasi-local-density approximation. We have found that, especially for larger ensembles (larger M), the present KLI ensemble energies are very close to the experimental values.

Table 2 presents the eigenenergies and the excitation energies. Note that the present KLI method gives a remarkably good approximation to the eigenenergies. This is especially true for the higher excited states. For the ground state the KLI is not so good (but still much better than the quasi-local values). This also means that the correlation energy is smaller for the higher excited states than for the ground state. KLI gives a worse result for the first excited state than the Hartree–Fock method [27].

Table 1. He ensemble energies $\mathcal{E}(M_I)$ and ensemble energy differences $\Delta\mathcal{E}(M_I) = \mathcal{E}(M_I) - \mathcal{E}(M_{I-1})$ calculated using both the quasi-local-density approximation and the KLI (present) method, compared with the corresponding experimental values (in Ry).

I	State	M_I	$\mathcal{E}(M_I)^{\text{GOK}}$	$\mathcal{E}(M_I)^{\text{KLI}}$	$\mathcal{E}(M_I)^{\text{exp}}$	$\Delta\mathcal{E}(M_I)^{\text{GOK}}$	$\Delta\mathcal{E}(M_I)^{\text{KLI}}$	$\Delta\mathcal{E}(M_I)^{\text{exp}}$
1	1S	1	-5.672	-5.723	-5.807			
2	2S	5	-4.452	-4.563	-4.630	1.2398	1.1606	1.1770
3	2P	17	-4.111	-4.332	-4.370	0.3458	0.2307	0.2601
4	3S	21	-4.070	-4.291	-4.325	0.0406	0.0408	0.0450
5	3P	33	-3.990	-4.223	-4.249	0.0829	0.0681	0.0765
6	3D	53	-3.925	-4.178	-4.197	0.0670	0.0452	0.0518
7	4S	57	-3.917	-4.170	-4.188	0.0082	0.0079	0.0088
8	4P	69	-3.896	-4.151	-4.166	0.0200	0.0190	0.0215

Table 2. He energies and excitation energies calculated with the quasi-local-density approximation and the KLI (present) method, compared with the corresponding experimental values (in Ry).

I	E^{GOK}	E^{KLI}	E^{HF}	E^{exp}	ΔE^{GOK}	ΔE^{KLI}	ΔE^{HF}	ΔE^{exp}
1	-5.672	-5.723	-5.723	-5.807				
2	-4.147	-4.273	-4.346	-4.336	1.525	1.451	1.377	1.471
3	-3.969	-4.236		-4.262	1.703	1.487		1.545
4	-3.894	-4.117		-4.132	1.778	1.607		1.675
5	-3.850	-4.104		-4.116	1.822	1.619		1.691
6	-3.818	-4.103		-4.111	1.854	1.620		1.696
7	-3.811	-4.065		-4.068	1.861	1.658		1.739
8	-3.795	-4.059		-4.060	1.877	1.664		1.747

The ensemble energy (3) depends on the weighting factors w_k . The excitation energies, however, are independent of w_k provided that the exact ensemble Kohn–Sham potential is used. In the exchange-only case, however, there is a slight dependence on the weighting factors w_k . Considering, for instance, the ensemble constructed from the ground and the first excited states

$$\mathcal{E} = (1 - w)E_1 + wE_2 \quad (42)$$

the first excitation energy is given by

$$\Delta E = E_2 - E_1 = \frac{\mathcal{E} - E_1}{w}. \quad (43)$$

The first derivative of ΔE with respect to w disappears:

$$\begin{aligned} \frac{\partial(\Delta E)}{\partial w} &= \sum_j \int \left(\frac{\delta(\Delta E)}{\delta u_j^*} \frac{\partial u_j^*}{\partial w} + \text{c.c.} \right) \text{d}\mathbf{r} = \sum_j \epsilon_j \int \left(u_j^* \frac{\partial u_j}{\partial w} + u_j \frac{\partial u_j^*}{\partial w} \right) \text{d}\mathbf{r} \\ &= \sum_j \epsilon_j \frac{\partial}{\partial w} \int |u_j|^2 \text{d}\mathbf{r} = 0, \end{aligned} \quad (44)$$

where the Kohn–Sham equations and the normalization of the Kohn–Sham orbitals were used. Thus the dependence of the excitation energies on the weighting factors is of second or higher order.

Table 3 shows the first excitation energy determined for several values of the weighting factor w . For comparison the Hartree–Fock [27] values are also presented. The Hartree–Fock first excitation energy is worse than the KLI value, although the first-excited-state energy is better predicted by the Hartree–Fock than the KLI method. In the previous generalized KLI approximation [26] denoted by KLI* in table 3, there is a linear dependence on the weighting

Table 3. First excitation energy (in Ry) of the He atoms for several values of the weighting factor w .

w	Electron configuration	KLI	KLI*	HF	GOK	Expt
0.05	$1s^{1.8}2s^{0.2}$	1.489	0.918			
0.10	$1s^{1.6}2s^{0.4}$	1.480	1.020			
0.15	$1s^{1.4}2s^{0.6}$	1.469	1.138			
0.20	$1s^{1.2}2s^{0.8}$	1.451	1.265	1.377	1.525	1.471

factor in the excitation energy. The fact that in the present KLI method there is only a slight dependence on w means that the present version of the ensemble KLI is more appealing.

The derivation of the ensemble KLI approximation goes exactly the same way as in the ground state and the form of the KLI potential is also the same. As the KLI is so successful for the ground state we might expect the same for the ensemble state. The results presented here are in accord with this expectation.

The calculations discussed in this paper are exchange-only calculations. The inclusion of correlation is straightforward in principle. One only needs a correlation functional as a functional of the orbitals and then the methods used for the derivation and calculation are exactly the same. Unfortunately, we do not have ensemble correlation functionals. In ground-state theory finding an appropriate correlation functional, i.e. a correlation functional that performs well together with the KLI exchange, is a fundamental problem. In the existing approximating functionals exchange and correlation are treated together and if we change only the exchange part (into KLI) the balance between the exchange and correlation is ruined and we might receive worse results than in the exchange-only case. Gross and co-workers [29] found that the Colle–Salvetti correlation functional is the best. In a lot of cases KLI + Colle–Salvetti functional gives better results than any other. It is possible that the KLI + Colle–Salvetti approximation will also be appropriate for the ensemble states, or, for example, correlation functionals arising from second-order perturbation theory.

The development of modern density functionals is becoming increasingly fundamental in the sense that a great variety of known exact properties have to be fulfilled by a density functional. There are a great number of papers on this concerning ground-state theory [30–33]. Recently, there has been growing interest in finding such exact properties in the time-dependent case [16,34]. For the ensemble excited-states theory there are only a couple of papers covering this topic [14,35,36].

We would like to emphasize that ensemble calculations are only slightly more complicated than ground-state calculations and thus ensemble calculations can be routinely performed just like ground-state calculations. These can be regarded as rivalling the powerful time-dependent density-functional approach for the calculation of excitation energies. The practical troubles one has to face in dealing with bigger systems are exactly the same as in the ground state. (For a recent review of ground-state OPM and KLI calculations see [29].)

Acknowledgments

This work was supported by OTKA grant no T029469. The grant ‘Széchenyi’ from the Hungarian Ministry of Culture and Education is gratefully acknowledged.

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