Excited-state density functional calculations on the helium isoelectronic sequence

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Abstract. Self-consistent density-functional calculations, in an exchange-only framework, are reported for the energies and moments of the $2\,^3S$ excited states of the helium isoelectronic sequence, according to the prescription of Harbola and Sahni. The total energy values show excellent agreement with "exact" nonrelativistic values while the moments are also quite satisfactory.

Keywords. Self-consistent density-functional calculations; helium isoelectronic sequence; exchange-only framework.

1. Introduction

Since 1964, density functional theory (DFT) has enjoyed remarkable successes in vividly explaining the electronic structure, binding and properties of atoms, molecules, clusters and solids in their ground states (Bamzai and Deb 1981; March and Deb 1987; Parr and Yang 1989; Kryachko and Ludena 1990; Trickey 1990; Labanowski and Andzelm 1991). However, one of the major unsolved problems in DFT has been its inability to satisfactorily deal with excited states. Because of this, large areas in spectroscopy and molecular reaction dynamics (where both time-dependence and excited states are involved) have remained outside the purview of DFT.

There are several reasons for DFT's discomfiture concerning excited states:

(1) There is no Hohenberg–Kohn theorem for a general excited state of a many-electron system, since in this case the wave function cannot be bypassed through the pure-state density. This is apparent from the hydrodynamical form of the wave function in terms of the density and the phase function (Deb and Ghosh 1987). The latter is not constant for a general excited state.

(2) Exact functional forms of the kinetic energy (T) and exchange-correlation energy (E_{xc}) in terms of the density are still unknown. In particular, $E_{xc}[\rho]$ for an excited state need not have the same functional dependence on density as for the ground state.

(3) Abandoning the concept of a state function within DFT and working solely in terms of single-particle densities is advantageous for the ground state but disadvantageous for excited states. One loses linear superposition and encounters nonlinearity.

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(4) The very complicated problem of ensuring Hamiltonian and wave-function orthogonalities which is faced by any variational method: In other words, for an excited state, its overlap matrix element and the Hamiltonian matrix element with any lower state must vanish. This is outside the orthogonality requirement automatically satisfied by the space and spin symmetry of the states.

In §2, we first briefly review the salient features of the main attempts (Slater 1974; Theophilou 1987; Gross *et al* 1989; Harbola and Sahni 1989, 1992; Koga 1990, 1991; Sen and Harbola 1991; Sen 1992) for a DFT calculation of excited-state energies and densities. This is necessary because although we still do not have a viable excited-state DFT, success may eventually come from similar methods or perhaps a combination of such methods. This section also describes briefly the Harbola–Sahni approach which has the potential of being applicable to excited states. Section 3 discusses our computed results on the $2\,^3S$ states of the helium isoelectronic sequence by using the Harbola–Sahni (1989, 1992) method. Finally, §4 makes a few concluding remarks.

2. An overview of some excited-state DFT calculations

2.1 *The ensemble density approach*

The first step towards a DFT for excited states came around 1970, with Slater's (1974) transition-state theory. Here, the equations were exactly like the Kohn–Sham equations (see, e.g., Parr and Yang 1989), but the density was assumed to correspond to a fictitious *transition state* in which one or more orbitals are fractionally occupied. Theophilou (1987) showed that there is a rigorous justification of Slater's theory, where the fractional occupation numbers are derived rigorously. But, instead of corresponding to a single state of the many-electron system, the density actually is the sum of M lowest-energy eigenstate densities, with equal weightage. This is the *equiensemble* concept. Thus, information about the Mth eigenstate is obtained by solving *two* sets of Kohn–Sham equations, one set for the M and one set for the $(M-1)$ lowest-energy eigenstate densities.

An important drawback of the transition-state approach is that it assumes the XC potentials for ground and excited states to have the same functional dependence on electron density.

In a generalization and extension of Theophilou's approach, Gross *et al* (1989) derived a Rayleigh–Ritz variational principle for more general ensembles in which the lowest M eigenstates are weighted unequally. For non-interacting systems, these ensembles correspond to fractionally occupied single-particle states. This approach leads to an *exact* expression relating the excitation energies to the Kohn–Sham eigenvalues. However, approximations must be invoked in order to make this *formally* exact relation practical for computation. Gross *et al* (1989) have extended their treatment to *arbitrarily* large ensembles including degenerate states.

However, numerical calculations according to the above approach have not been very encouraging. Thus, in an application to the He atom Gross *et al* (1989a) observed that the calculated (i) excitation energies are typically wrong by about 20% and (ii) radial density for the 4F state $(1s4f)$ is not satisfactory.

2.2 The local scaling transformation method

This method, devised by Kryachko and Ludena (1990), Koga (1990, 1991) and others, consists of the following features for the *ground state*.

(a) Start from a reference N-electron wave function $\Psi_0(r_1, \cdots, r_N)$ corresponding to a reference electron density $\rho_0(r)$.

(b) Generate an N-electron wave function $\Psi_\rho(r_1, \cdots, r_N)$ from a given (trial) electron density $\rho(r)$ through a unique one-electron transformation T, where $\rho(r) = T\rho_0(r)$.

(c) If $\rho(r)$ contains adjustable parameters, then these would enter into Ψ_ρ, enabling one to variationally optimize the parameters.

(d) Even if one uses a trial density $\rho(r)$ which is considerably simpler than the Hartree–Fock (HF) density, the method can deliver atomic density and energy of near-HF accuracy.

The advantages of this approach are: (1) Simplicity and accuracy in the calculated density and energy. (ii) Retention of the wave-function concept within DFT (hence, this may be applicable to excited states). (iii) Improvement of an approximate wave function $\Psi_\rho(r_1, \cdots, r_N)$. The disadvantages of this approach are: (i) This may not be regarded as a genuine first-principles method. Here, one needs to work with Ψ_0, ρ_0, ρ and Ψ_ρ. Actually, this method improves Ψ_0 and ρ_0, and does not obtain an unknown Ψ. (ii) The adjustable parameters in Ψ_ρ are to be optimized through multivariate nonlinear optimization. This may be quite tedious. Still, this is a clever method.

For an *excited state*, the following steps are to be taken (Koga 1991).

(a) Use a configuration-interaction (CI)-type reference wave function.

(b) Choose a trial density $\rho(r)$ which approximates the nth-state density (of interest). Generate all the lower mth-state wave functions $\{\Psi_{m,\rho}\}$, $m \leqslant n$, in such a manner that the following wave-function and Hamiltonian orthogonalities are satisfied:

$$\langle \Psi_{n,\rho} | \Psi_{m,\rho} \rangle = \delta_{mn}, \tag{1}$$

$$\langle \Psi_{n,\rho} | H | \Psi_{m,\rho} \rangle = E_n(\rho)\delta_{mn}. \tag{2}$$

(c) Determine the nth-state density $\rho(r)$ so as to minimize the energy density functional defined through $\Psi_{n,\rho}$, *viz.*

$$E_n(\rho) = \langle \Psi_{n,\rho} | H | \Psi_{n,s} \rangle / \langle \Psi_{n,\rho} | \Psi_{n,\rho} \rangle. \tag{3}$$

It is clear from the above description that in this procedure the choice of a good Ψ_0 is very important. Then, this can be improved further, keeping the density relatively simple. In Koga's calculation on the $2\,^1S$ state of the He atom, the computed radial density agreed to within 0·005, the energy to within 0·09%, $\langle r^4 \rangle$ to within 1·73% and $\langle r^{-2} \rangle$ to within 0·07%, with the corresponding "exact" results.

3. The Harbola–Sahni approach within the local density approximation

The Kohn–Sham (KS) DFT equations (Parr and Yang 1989) may be written as (atomic units employed, es = electrostatic)

$$[-\tfrac{1}{2}\nabla^2 + V_{es}(r) + W_{xc}(r)]\,\psi_i(r) = \varepsilon_i \psi_i(r), \tag{4}$$

$$\rho(\mathbf{r}) = \sum_i |\psi(\mathbf{r})|^2. \tag{5}$$

Harbola and Sahni (HS) (1989, 1992) proposed that the effective local XC potential (W_{xc}) that the electrons move in can be obtained by calculating the work done in moving an electron in the electric field of its Fermi–Coulomb hole-charge distribution. Thus, $W_{xc}(\mathbf{r})$ is given by the line integral

$$W_{xc}(\mathbf{r}) = -\int_\infty^r \varepsilon_{xc}(\mathbf{r}') \cdot d\mathbf{l}, \tag{6}$$

$$\varepsilon_{xc}(\mathbf{r}) = \int \frac{\rho_{xc}(\mathbf{r}, \mathbf{r}')(\mathbf{r} - \mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|^3} \, d\mathbf{r}'. \tag{7}$$

$\varepsilon_{xc}(\mathbf{r})$ is the electric field for an electron at $\mathbf{r}$ due to the Fermi–Coulomb hole-charge density $\rho_{xc}(\mathbf{r}, \mathbf{r}')$ at $\mathbf{r}'$.

If only exchange is considered (i.e., no correlation), then

$$\rho_x(\mathbf{r}, \mathbf{r}') = \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{2\rho(\mathbf{r})}, \tag{8}$$

$\gamma(\mathbf{r}, \mathbf{r}') = $ single-particle density matrix

$$= \sum_i \psi_i^*(\mathbf{r})\psi_i(\mathbf{r}'); \{\psi_i(\mathbf{r})\} \equiv \text{orbitals}. \tag{9}$$

For spherically symmetric systems, the line integral in (6) is reduced to an integral over the radial coordinate only.

This interpretation of W_{xc} is similar in spirit to the interpretation of the Hartree electrostatic potential $V_{es}(\mathbf{r})$. The XC energy is thus the interaction energy between the electron density and the Fermi–Coulomb hole charge.

In order that the potential is well-defined, the work done must be path-independent, i.e., $\nabla \times \varepsilon_{xc}(\mathbf{r}) = 0$. This is automatically true for spherically symmetric systems. For non-spherical systems, an *approximate* potential can be obtained from the longitudinal (curl-free) component of the electric field.

Although one solves KS equations with this $W_{xc}(\mathbf{r})$, the KS $W_{xc}(\mathbf{r})$ and the HS W_{xc} (r) are *not* equivalent. The KS scheme is variational while the HS scheme is *non-variational*. Therefore, the latter may be employed for excited states, assuming that a local XC potential exists for the excited states. The first excited-state calculations were done by Sen (1992) for Be and Na, using single-determinantal wave functions, in an exchange-only framework. The next such calculation appears to be ours, in the present paper.

The HS approach essentially gives a prescription based on the physics of interaction between charges and does not involve any explicit functional form. Therefore, within a local density approximation, this prescription may be regarded as universal, since it admits the possibility that W_{xc} may have different functional dependence upon the density for different excited states.

4. The helium isoelectronic sequence: Results and discussion

In our laboratory, we have set up a computer program for numerically obtaining self-consistent solutions of KS-type equations for atomic systems, for any effective local potential, of which the HS potential is one example. The code of Herman and Skillman (1963) has been suitably modified to incorporate the given effective potential. The same program has been used to calculate ground-state properties of atoms as well as the $2\,^3S(1s2s)$ excited states of He and other members of its isolectronic series (up to Ne^{8+}), using the HS prescription.

Table 1 compares our calculated results in an exchange-only framework for He, Li and Be with those of Harbola and Sahni (1992). For He, our results for total energy, the highest occupied orbital energy and moments $\langle r \rangle$, $\langle r^2 \rangle$, $\langle r^{-1} \rangle$, $\langle r^{-2} \rangle$, agree very well with the HF and HS results. In contrast to the HS results, our results are not *identical* to the HF ones for He although they are very close. The largest discrepancy is observed for the highest occupied orbital energy and the moment $\langle r^{-2} \rangle$, our values being smaller in magnitude. All our computations have been performed in double precision and the wave function has been normalized up to the 15th decimal place. Note that for Li and Be our total energy values are closer to the HF ones. With an increase in the numerical accuracy of computations, this situation should improve further.

Table 2 reports the energy values for the $2\,^3S$ states of the He isoelectronic sequence. The "exact" values (Thakkar and Smith 1977), shown for comparison, incorporate electron correlation whereas our results do not. It is quite gratifying that our calculated total energies are in error only to the extent of 0·08 to 0·0002%. Since the core orbital shrinks progressively due to increasing nuclear charge, the effects of electron correlation for this excited state would decrease along the isoelectronic sequence. In other words, agreement of our results with the "exact" ones is expected to be worst for He and to improve along the sequence up to Ne^{8+}. This is what is by and large

Table 1. Comparison between our results and those of Harbola and Sahni (1992), for total energy, highest occupied orbital energy and the moments $\langle r \rangle$, $\langle r^2 \rangle$, $\langle r^{-1} \rangle$, $\langle r^{-2} \rangle$, for the ground states of He, Li, and Be atoms. The energies are in rydbergs while the moments are in atomic units. (PW = present work, HS = Harbola-Sahni).

| Atom | Total energy -E | | Highest occupied orbital energy | | $\langle r \rangle$ | $\langle r^2 \rangle$ | $\langle r^{-1} \rangle$ | $\langle r^{-2} \rangle$ |
	PW	HS	PW	HS				
He	5·7232	5·724	−1·781	−1·836	0·9272	1·1846	1·6873	5·9822
	(5·724)[a]		(−1·836)[a]		(0·9273)[b]	(1·1848)[b]	(1·6873)[b]	(5·9955)[a]
Li	14·8656	14·864	−0·373	−0·405	1·6321	5·8557	1·9074	10·0348
	(14·866)[a]		(−0·393)[a]		(1·6320)[b]	(5·8541)[b]	(1·9073)[b]	(10·0624)[b]
Be	29·1432	29·142	−0·592	−0·626	1·5140	4·2213	2·1041	14·3411
	(29·146)[a]		(−0·619)[a]		(1·5140)[b]	(4·2211)[b]	(2·1040)[b]	(14·3918)[b]

[a]Hartree–Fock results; [b]taken from Harbola and Sahni (1992)

Table 2. Total energy (in rydbergs) and $(-V/T)$ values for the $2\,^3S$ states of the He isoelectronic sequence. The "exact" values are from Thakkar and Smith (1977). Values in parentheses denote percent errors.

Atom/ion	Total energy (-E)		$-V/T$
	Present work	"Exact"	
He	4·3469 (0·08)	4·3505	1·99998
Li$^+$	10·2177 (0·04)	10·2215	2·00001
Be^{2+}	18·5895 (0·03)	18·5943	1·99998
B^{3+}	29·4624 (0·02)	29·4678	1·99998
C^{4+}	42·8358 (0·01)	42·8415	·1·99999
N^{5+}	58·7094 (0·01)	58·7154	1·99998
O^{6+}	77·0923 $(-0·004)$	77·0893	2·00003
F^{7+}	97·9630 (0·0002)	97·9632	1·99994
Ne^{8+}	121·3350 (0·002)	121·3373	1·99995

Table 3. Expectation values (a.u.) of single-particle operators r, r^2, r^{-1}, r^{-2} for the $2\,^3S$ states of the He isoelectronic sequence. For He, the corresponding accurate results from Thakkar and Smith (1977) are given in parentheses.

Atom/ion	$\langle r \rangle$	$\langle r^2 \rangle$	$\langle r^{-1} \rangle$	$\langle r^{-2} \rangle$
He	2·5117	11·0958	1·1559	4·1548
	(2·5505)	(11·4641)	(1·1547)	(4·1705)
Li$^+$	1·4814	3·7046	1·7815	9·5623
Be^{2+}	1·0576	1·8583	2·4064	17·2052
B^{3+}	0·8236	1·1172	3·0314	27·0806
C^{4+}	0·6747	0·7457	3·6563	39·1850
N^{5+}	0·5715	0·5330	4·2813	53·5159
O^{6+}	0·4958	0·4001	4·9067	70·0807
F^{7+}	0·4378	0·3113	5·5317	88·8570
Ne^{8+}	0·3920	0·2491	6·1565	109·8477

observed in table 2. The ratio $(-V/T)$ is exactly 2, according to the virial theorem; this is also satisfied well in our computations. However, the energy of O^{6+} has gone slightly below the "exact" nonrelativistic value, probably indicating a minor numerical error. Note that O^{6+}, F^{7+} and Ne^{8+} manifest the worst agreement with the virial theorem. However, taken together, the energy values may be regarded as excellent.

Table 3 reports the moments, $\langle r \rangle$, $\langle r^2 \rangle$, $\langle r^{-1} \rangle$, $\langle r^{-2} \rangle$, for the $2\,^3S$ states of the isoelectronic sequence. For He, the comparison with more accurate results (including electron correlation, Thakkar and Smith 1977) shows that, for the higher moments $\langle r^2 \rangle$, $\langle r^{-2} \rangle$, our exchange-only results have 3·2 to 0·5% error respectively, while the lower moments show better agreement. The radial densities for all the systems are shown in figure 1.
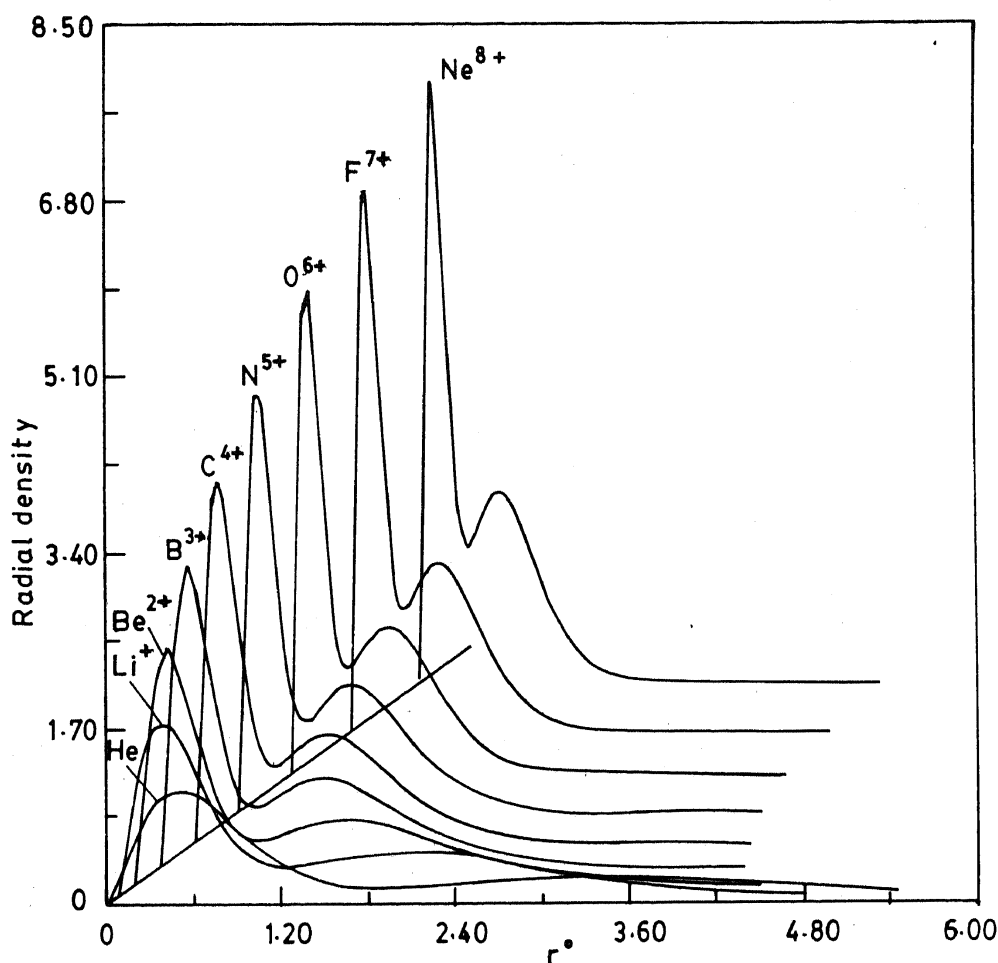
Figure 1. Radial densities in the $2\,^3S$ states of the He isoelectronic sequence. All values are in atomic units.

5. Conclusion

The present calculations and those of Sen (1992) indicate that the HS prescription for the XC potential has considerable potential for excited states. However, so far the method has been applied to spherically symmetric systems, with single-determinantal wave functions. Further work is necessary before the approach can be extended to even ground states of diatomic molecules. Excited states of molecules and multideterminantal wave functions would require other modifications.

References

Bamzai A S and Deb B M 1981 *Rev. Mod. Phys.* **53** 95, 593

Deb B M and Ghosh S K 1987 In *The single-particle density in physics and chemistry* (eds) N H March and B M Deb (London: Academic Press)

Gross E K U, Oliveira L N and Kohn W 1989 *Phys. Rev.* **A37** (a) 2805, (b) 2821

Harbola M K and Sahni V 1989 *Phys. Rev. Lett.* **62** 489

Harbola M K and Sahni V 1992 *Phys. Rev.* **A45** 1434

Herman F and Skillman S 1963 *Atomic structure calculations* (Englewood Cliffs, NJ: Prentice-Hall)

Koga T 1990 *Phys. Rev.* **A41** 1274

Koga T 1991 *J. Chem. Phys.* **95** 4306

Kryachko E S and Ludena E V 1990 *Energy density functional theory of many-electron system* (Dordrecht: Kluwer Academic Press)

Labanowski J K and Andzelm J W (eds) 1991 *Density functional methods in chemistry* (New York: Springer-Verlag)

March N H and Deb B M 1987 *The single-particle density in physics and chemistry* (London: Academic Press)

Parr R G and Yang W 1989 *Density-functional theory of atoms and molecules* (Oxford: University Press)

Sen K D 1992 *Chem. Phys. Lett.* **188** 510

Sen K D and Harbola M K 1991 *Chem. Phys. Lett.* **178** 347

Slater J C 1974 *The self-consistent fields for molecules and solids* (New York: McGraw-Hill)

Thakkar A J and Smith V H Jr 1977 *Phys. Rev.* **A15** 16

Theophilou A K 1987 In *The single-particle density in physics and chemistry* (eds) N H March and B M Deb (London: Academic Press)

Trickey S B (ed.) 1990 *Density-functional theory of many-Fermion systems: Advances in quantum chemistry*, vol. 21 (New York: Academic Press)