

Accuracy of the Hartree-Fock and Local Density Approximations for Electron Densities: A study for Light Atoms

C. -O. Almbladh, U. Ekenberg, and A. C. Pedroza

Department of Theoretical Physics, University of Lund, Sölvegatan 14A, S-22 362 Lund, Sweden

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Abstract

We compare the electron densities and Hartree potentials in the local density and the Hartree-Fock approximations to the corresponding quantities obtained from more accurate correlated wavefunctions. The comparison is made for a number of two-electron atoms, Li, and for Be. The Hartree-Fock approximation is more accurate than the local density approximation within the 1s shell and for the spin polarization in Li, while the local density approximation is slightly better than the Hartree-Fock approximation for charge densities in the 2s shell. The inaccuracy of the Hartree-Fock and local density approximations to the Hartree potential is substantially smaller than the inaccuracy of the local density approximation to the ground-state exchange-correlation potential.

1. Introduction

For atoms and for molecules of moderate size, configuration interaction (CI) offers a powerful method for obtaining accurate solutions to the many-electron problem [1]. Both the ground state and the excited states can be treated by this method. For the lightest atoms such as He and Li very accurate results have been obtained using Hylleraas-type wavefunctions [1], but this method is not tractable for larger systems. For solids on the other hand, methods like CI involve conceptual and practical problems which have so far not been solved.

For systems with a macroscopic number of particles such as solids, one usually resorts to field-theoretical formulations of the many-body problem in order to obtain excitation energies. Ground-state properties, such as the ground state energy, the electron density, or vibrational frequencies, can be obtained using the simpler density functional theory by Hohenberg, Kohn, and Sham [2, 3]. In most applications of the density-functional theory the local density (LD) approximation is used, where one approximates the universal exchange-correlation functional E_{xc} by

$$E_{xc}[\rho] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho(\mathbf{r})) d^3r \quad (1)$$

Here $\epsilon_{xc}(\rho)$ is the exchange-correlation energy of the homogeneous electron gas at density ρ . This approximation is exact in the limit of very slowly varying densities but it has no *a priori* justification when the density is as rapidly varying as it is in a real atom, molecule or solid. A great number of calculations have demonstrated, however, that this approximation is able to give quantitative or semiquantitative results for such systems [4].

Both for obtaining ground-state properties and for obtaining excitation energies it is of importance to have an accurately determined electronic charge density $\rho(\mathbf{r})$. For an atom or a molecule, this can be obtained using e.g. CI, but for a solid the LD approximation is the most widely used method. There are however also a number of Hartree-Fock (HF) studies, mostly

for ionic solids. The density determines the electrostatic or Hartree potential

$$V_H(\mathbf{r}) = \int \rho(\mathbf{r}') v(\mathbf{r} - \mathbf{r}') d^3r' \quad (2)$$

which is a dominating term in the Dyson's equation

$$[-\frac{1}{2}\nabla^2 + w + V_H + \Sigma(E_i)] \chi_i(E_i) = E_i \chi_i(E_i) \quad (3)$$

for the excitation energies of the system. (In eq. (2) $v(\mathbf{r}) = 1/r$ is the interparticle interaction, in eq. (3) w is the external potential from the nuclei, $\Sigma(E)$ is the non-local and non-Hermitian self-energy, and $\chi_i(E)$ is a quasiparticle amplitude. We use atomic units such that $\hbar = e^2 = m = 1$.) In a ground-state calculation the density gives the total electronic electrostatic energy $(1/2) \int \rho V_H d^3r$, a term which is normally much larger than the exchange-correlation energy. It would be of limited value to improve the approximations for the self-energy or for the exchange-correlation energy if the dominating error due to a poor $\rho(\mathbf{r})$ lies in V_H .

The aim of the present paper is to give a comparison between charge densities and Hartree potentials in the Hartree-Fock and local density approximations and the corresponding exact quantities for systems where these exact quantities are available. A study of total energies of two-electron systems in local-density-type approximations and their accuracy has been made by Larsson and Calais [5], and a study for the He atom has been presented by Smith et al. [6]. The systems that we have studied are the two-electron systems H^- , He, Li^+ , and Be^{2+} ; one three-electron system (Li), and one four-electron system (Be). Given the exact densities it is also possible to construct the exact ground-state exchange-correlation potential $v_{xc}(\mathbf{r})$. How this is done will be described in a subsequent paper [7]. The correlated densities we have used were calculated by Larsson [8], Larsson and Smith [9], and by Bunge [10]. In the next section we present the numerical results, and in Section 4 we give our conclusions.

2. Details of the calculations

The correlated densities for H^- , He, Li^+ [8] and for Li [9] were constructed from wavefunctions of Hylleraas form. The accuracy of the Li wavefunction [9] we used is not as good as, e.g., that from an earlier calculation by Larsson [11], but the latter wavefunction or the program for recomputing it is no longer available. The total energy and the value of the spin densities at the nucleus of the wavefunction in [9] suggest, however, that the data are of high enough accuracy for our purpose. The wavefunctions for Be^{2+} and Be were calculated

Table I. The total energy of the correlated wave functions used in this work. Atomic units

H ⁻	-0.527 750
He	-2.903 724
Li ⁺	-7.279 912
Be ²⁺	-13.655 295
Li	-7.467 636
Be	-14.666 902

by Bunge [10] by the CI method and are of high accuracy. As a measure of the accuracy we give the total energies of the correlated wavefunctions in Table I. The errors in our correlated densities are sufficiently small compared to the errors in the LD or HF densities that they can be regarded as exact in our comparison below.

The HF and LD densities were obtained in a standard way by numerically solving radial Schrödinger equations rather than using basis sets. The densities for neutral Li were obtained using the unrestricted HF and the local density approximation to the spin density functional theory [12], respectively.

In the density-functional theory one obtains the density from SCF equations³

$$[-\frac{1}{2}\nabla^2 + w + V_H + v_{xc}] \psi_i = \epsilon_i \psi_i \quad (4)$$

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} |\psi_i(\mathbf{r})|^2 \quad (5)$$

where $v_{xc}(\mathbf{r}) = \delta E_{xc}[\rho]/\delta \rho(\mathbf{r})$. In the LD approximation, (eq. 1), we have simply

$$v_{xc}(\mathbf{r}) = \mu_{xc}(\rho(\mathbf{r})) \quad (6)$$

where $\mu_{xc}(\rho) = d(\rho \epsilon_{xc})/d\rho$. We recall that the orbitals ψ_i and eigenvalues ϵ_i are just auxiliary quantities used for constructing $\rho(\mathbf{r})$ and the total energy and that they normally do not have any clear physical meaning of their own [13].

In the local density approximation to the spin-density formalism one approximates E_{xc} by

$$E_{xc}[\rho^+, \rho^-] = \int \rho(\mathbf{r}) \epsilon_{xc}(\rho^+(\mathbf{r}), \rho^-(\mathbf{r})) d^3r \quad (7)$$

where $\rho^\pm$ are local spin densities, $\rho = \rho^+ + \rho^-$, and ϵ_{xc} is the exchange-correlation energy of the spin-polarized electron gas. The exchange-correlation potential is in this case spin-dependent and a function of the local spin densities:

$$v_{xc}^\pm(\mathbf{r}) = \{d[\rho \epsilon_{xc}(\rho^+, \rho^-)]/d\rho^\pm\}_{\rho^\pm = \rho^\pm(\mathbf{r})} \quad (8)$$

The exchange-correlation energies needed in the LD calculations were obtained by parametrizing the Monte-Carlo result by Ceperley and by Ceperley and Alder [15]. An earlier parametrization (see Williams and von Barth [4]) based on electron gas data by Singwi et al. [16] was also used and gave very similar density profiles.

We conclude this section by some remarks in the H⁻ case. Here the HF and LD approximations fail, in two different ways. We denote the total HF and LD energies by $E_{\text{HF}}(n)$ and $E_{\text{LD}}(n)$, n being a (possibly fractional) occupation number. For H and H⁻, $E_{\text{HF}}(1) = -0.5$ a.u. and $E_{\text{HF}}(2) = -0.4879$ a.u. The H⁻ ion is thus unstable in the Hartree-Fock approximation. The HF 1s energy eigenvalue is negative, however, and a *restricted* HF solution with correct boundary condition can be obtained.

The LD approximation fails for H⁻ in a different way. Here a solution with correct boundary conditions to the variational problem ($\delta E = 0$) does not exist when $n = 2$. The energy functional to be minimized has however a well-defined infimum or "greatest lower bound" (glb) which we denote by $E_{\text{LD}}(2)$. The failure can be demonstrated by performing LD calculations with fractional occupation numbers [17]. At $n = n_1 \simeq 1.7$, the energy eigenvalue $\epsilon(n)$ tends to zero. For $n > n_1$ the glb of the functional is $E_{\text{LD}}(n_1)$. This can be seen as follows. Let us enclose the system in a big quantization box. The most favorable density is to have n_1 electrons localized on the atom and the remaining electronic charge delocalized. $E_{\text{LD}}(n)$ is the glb of the LD energy functional of this system for all possible densities and box sizes. It readily follows that $E_{\text{LD}}(n) = E_{\text{LD}}(n_1)$ when $n > n_1$. Since $\epsilon(n) = \partial E/\partial n$ in density functional theory it follows that $E_{\text{LD}}(n_1)$ has a horizontal slope at the critical point $n = n_1$. It is amusing to notice that $E_{\text{LD}}(2) = -0.524$ a.u., in fair agreement with the experimental value -0.528 a.u.

In order to obtain an LD density profile for H⁻ we enclosed the system in a sphere of radius R and imposed boundary conditions $\psi(R) + \alpha \psi'(R) = 0$. The results are insensitive to R and to α for R in a wide range. The numerical results given in the next section refer to $R = 31.5$ a.u.

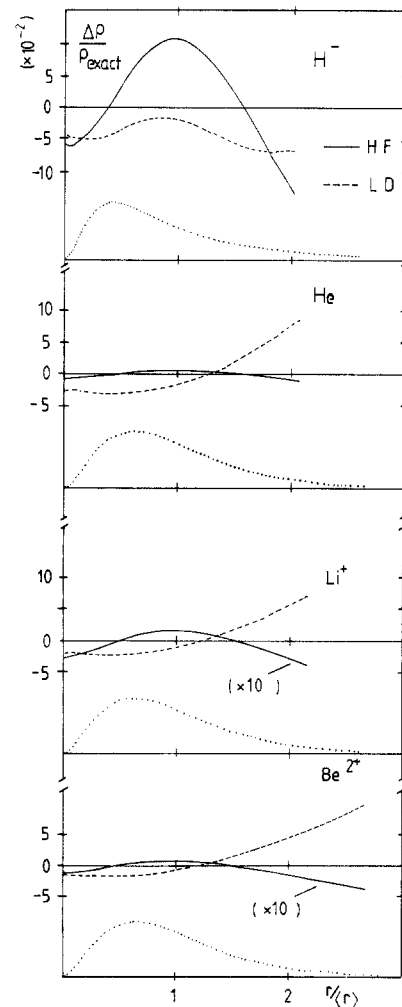


Fig. 1. The relative charge density difference $\Delta\rho/\rho_{\text{exact}}$ for H⁻, He, Li⁺, and Be²⁺. $\Delta\rho = \rho_{\text{HF,LD}} - \rho_{\text{exact}}$. The radial charge density $4\pi r^2$ (dotted) is also shown. The distance from the nucleus is measured in units of the first moment $\langle r \rangle$, where $\langle r \rangle$ is given in Table III.

Table II. Charge density at the nucleus $\rho(0)$

Atom	Exact	HF	LD
H ⁻	0.328	0.309	0.314
He	3.63	3.60	3.53
Li ⁺	13.71	13.67	13.44
Be ²⁺	34.40	34.36	33.86
Li	13.73	13.81	13.57
Be	35.37	35.39	34.86

3. Numerical results

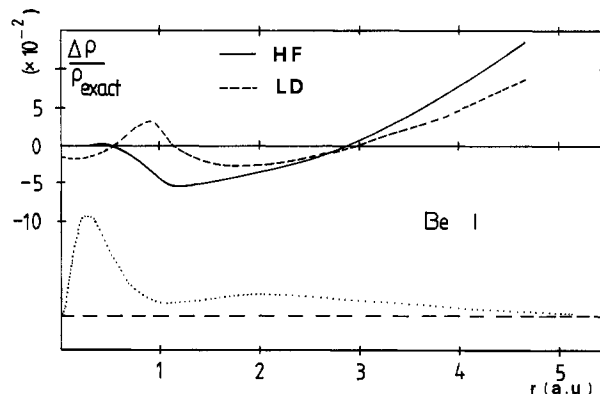
In Figs. 1–3 we show the relative charge density differences $\Delta\rho/\rho_{\text{exact}}$ where $\Delta\rho = \rho_{\text{HF,LD}} - \rho_{\text{exact}}$ in an obvious notation. The charge density $\rho(0)$ at the nucleus is given in Table II. For the two-electron systems He, Li⁺ and Be²⁺, HF gives densities very close to the exact densities. The LD approximation is not as good, giving relative deviations of the order 3% in regions with an appreciable particle density. Far out from the nucleus, the LD approximation gives densities which are too high. This may be due to the fact that the exact $v_{\text{xc}}(r) \sim -1/r - \alpha/(2r^4)$, when $r \rightarrow \infty$ [14], while in the LD $v_{\text{xc}} = \mu_{\text{xc}}(\rho(r)) \sim \exp(-\lambda r)$, $r \rightarrow \infty$. For H⁻ the finite-atom LD calculations gives a density which is slightly better than that obtained from HF theory.

In Table III we give moments $\langle r \rangle = \int \rho(r)r \, d^3r / \int \rho(r) \, d^3r$. These moments give primarily information on the outer part of the atom. For the two-electron atoms He, Li⁺, and Be²⁺ the Hartree-Fock moments are almost indistinguishable from the exact ones, while the LD moments are generally too large. The difference between the LD and the exact moments is also probably a consequence of the incorrect asymptotic behavior of the local-density approximation to v_{xc} .

We next turn to the four-electron system (Be) (Fig. 2). Within the 1s shell the HF density is very close to the exact density, while the LD approximation is less accurate ($\Delta\rho/\rho \sim 0.03$) (cf. also Table II). In the valence-electron region, however, the roles are reversed. Here the LD approximation still gives $|\Delta\rho/\rho| \sim 0.03$, while HF theory gives deviations about twice as big. In the valence-electron region correlation plays a more important role which explains why the HF approximation is less accurate. On the other hand the density is less rapidly varying and thus one expects that the LD approximation should work better. A related result has been obtained by von Barth [18], who found that for valence-electron shells the LD term splittings are more accurate than those obtained

Table III. Expectation values of r . For Li, partial expectation values corresponding to the two different spin directions (+, -) are also given

Atom	Exact	HF	LD
H ⁻	2.71	2.50	
He	0.929	0.927	0.959
Li ⁺	0.573	0.572	0.585
Be ²⁺	0.4143	0.4141	0.4207
+	2.22	2.22	2.21
Li -	0.58	0.57	0.59
av.	1.67	1.67	1.67
Be	1.494	1.532	1.522

Fig. 2. The relative charge density difference $\Delta\rho/\rho_{\text{exact}}$ for the neutral Be atom. The radial charge density $4\pi r^2 \rho$ (dotted) is also shown. Atomic units.

using HF theory. Table III shows that for Be, HF and LD approximations give moments of about the same accuracy.

In Fig. 3 we show the relative deviation in charge density and the deviation in “spin-split parameter” $x = (\rho^+ - \rho^-)/\rho$ for the neutral Li atom. Also in this case HF in the 1s region gives densities which are more accurate than the LD densities. At the density minimum between the 1s and 2s shells, the deviations reach their maxima both for HF and LD. The deviation in spin-split parameter (x) is for LD quite big here. The reason is that the LD 1s orbital is too extended, and thus $x(r)$ reaches its valence-electron value (≈ 1) at a slightly incorrect distance from the nucleus. In the valence-electron regime, the LD densities are comparable in accuracy to the HF densities. The moments $\langle r \rangle$ in Table III show no significant difference in accuracy between HF and LD approximations.

In Table IV we give values for the Fermi contact term $4\pi(\rho^+(0) - \rho^-(0))$ from the correlated wave function used in our comparison [9], the more accurate one in [11], LD, HF, and from experiment. The inaccuracy in the data from [9] is insignificant compared to the HF and LD inaccuracies. For the Fermi contact term LD theory gives a slightly better value than does (un-restricted) HF theory, but on an average HF is more accurate than LD in the 1s shell (Fig. 3).

We finally turn to the Hartree potentials V_{H} calculated from the exact, HF, and LD densities. We have found that HF is superior to LD in the 1s shell, while LD is as good as or slightly better than HF in the valence-electron region. It follows from elementary electrostatics that an inaccuracy in ρ within the 1s shell has little influence on the Hartree potential outside that shell. Consequently we expect that when we consider expectation values of V_{H} with respect to a valence-electron orbital, LD should be as good as or better than HF.

In Table V we give expectation values $\langle i|V_{\text{H}}|i \rangle$ of V_{H} calculated from the exact, HF, and LD densities. For definiteness we give expectation values with respect to HF orbitals $|i \rangle$. When we consider $\langle 1s|V_{\text{H}}|1s \rangle$, the Hartree-Fock approximation

Table IV. The Fermi contact term $4\pi(\rho^+(0) - \rho^-(0))$ for Li

Correlated	HF	LD	Experiment
2.915 ^a	2.823	2.861	2.906 ^c
2.906 ^b			

^a Computed from natural orbitals given in [9].

^b Ref. [11].

^c See Ref. [11].

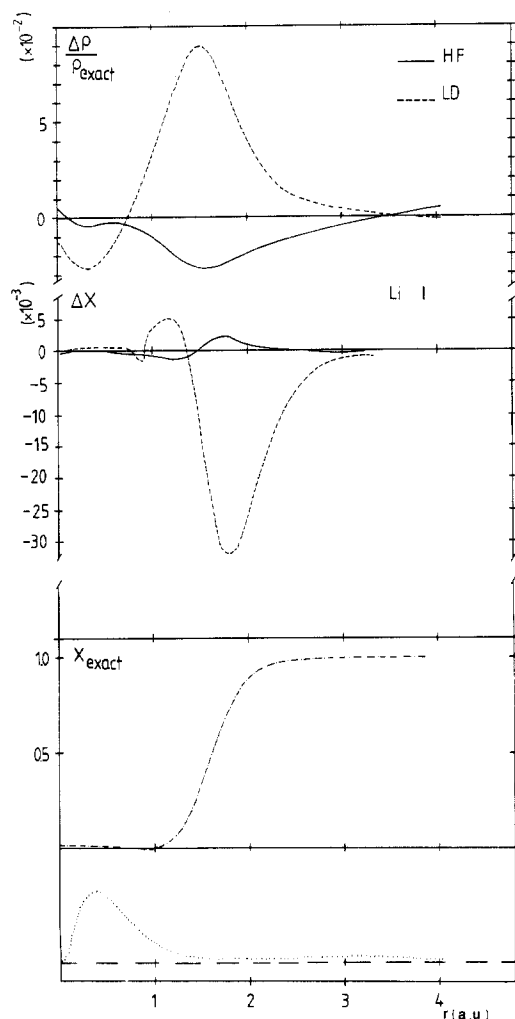


Fig. 3. Relative charge density difference $\Delta\rho/\rho_{\text{exact}}$ for Li (top); difference $\Delta x = x_{\text{HF,LD}} - x_{\text{exact}}$ in spin-split parameter for Li (center); and exact spin-split parameter $x(r) = (\rho^+(r) - \rho^-(r))/\rho$ for Li (bottom). The radial charge density $4\pi\rho r^2$ (dotted) is also shown. Atomic units.

to V_{H} is more accurate than the LD, as expected. When we consider expectation values with respect to valence orbitals, the LD approximation is slightly better than the HF approximation for Li and Be, giving errors in the milliHartree range. For the systems studied here, the LD approximation gives errors in $\langle i|v_{\text{xc}}|i\rangle$ which range from about 0.1 Hartree for the 2s orbital in Li to about 1 Hartree for the 1s orbitals in Be^{2+} and Be [7]. Thus for these systems the errors in V_{H} are insignificant compared to the errors in the local-density approximation to v_{xc} . It is conceivable that also the common approximations to Σ give uncertainties which are larger than the uncertainties in V_{H} found here.

4. Conclusions

In this paper we have compared charge densities and Hartree potentials for light atoms in the LD and HF approximation with the corresponding exact quantities. It appears to be a general belief that HF gives better densities than does the LD approximation, at least for atoms. For the atoms studied here this is true only within the 1s shell, while for Li and Be the LD approximation is as good as or slightly better than the HF approximation in the 2s shell.

As a measure of the uncertainty in the Hartree potential V_{H} due to the uncertainty in ρ , we have considered expectation values $\langle i|V_{\text{H}}|i\rangle$ with respect to HF orbitals $|i\rangle$. For a given valence-electron orbital $|i\rangle$, the LD and HF approximations give uncertainties in $\langle i|V_{\text{H}}|i\rangle$ of the order milliHartrees, which is substantially smaller than the error in the local-density approximation to v_{xc} . It seems likely that the theoretical uncertainties in the common approximation to the self-energy Σ also are larger than the very small uncertainty in the Hartree potential.

It is of course difficult to extrapolate the present experience to solid state or molecular calculations, but our findings give an indication that outside the core regions the LD and HF approximations give Hartree potentials which are more accurate than the present commonly used approximations to the self-energy Σ or the ground-state exchange-correlation potential v_{xc} .

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Table V. Expectation values of the Hartree potential with respect to the Hartree-Fock orbitals

	$\langle 1s V_{\text{H}} 1s\rangle$			$\langle 2s V_{\text{H}} 2s\rangle$			$\langle 2p V_{\text{H}} 2p\rangle$		
	Exact	HF	LD	Exact	HF	LD	Exact	HF	LD
H ⁻	0.776	0.791							
He	2.050	2.052	2.024						
Li ⁺	3.303	3.303	3.273	0.7834	0.7834	0.7824	0.7298	0.7298	0.7295
Be ²⁺	4.554	4.554	4.523	1.219	1.219	1.218	1.259	1.259	1.258
Li	3.640	3.627	3.600	0.8823	0.8789	0.8796			
Be	5.529	5.508	5.485	1.658	1.648	1.651	1.496	1.488	1.490

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