THE CORRELATED ELECTRON DENSITY OF THE Li ATOM – A TEST FOR DENSITY FUNCTIONALS AND SEMI-EMPIRICAL PSEUDOPOTENTIALS

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The contribution of core–valence correlation to the valence charge density of the Li atom has been calculated using (a) semi-empirical pseudopotentials adjusted to experimental ionization energies, and (b) a non-empirical density-functional correlation potential. The agreement with elaborate CI calculations is encouraging in both cases.

1. Introduction

Core–valence correlation plays an important role in determining properties of atoms and molecules with large, easily polarizable cores: it reduces e.g. electric dipole polarizabilities of alkali atoms by up to 40% [1]; bond lengths of alkali dimer ions X_2^+ decrease by up to 0.5 au [2]. It is rather difficult, on the other hand, to describe core–valence correlation effects accurately within the framework of configuration interaction (CI) methods, if large cores are involved [3].

While ab initio SCF pseudopotentials [4] exclude core–valence correlation from the beginning, it is implicitly introduced into semi-empirical pseudopotentials [5,6] through the fit to experimental data. Since the fit is to experimental *energies*, however, it is not clear if the influence of core–valence correlation on electron *densities* is accurately described within such a scheme. In this letter we try to answer this question for the most simple system, the Li atom.

We recently showed that reasonable estimates for total and valence correlation energies of atoms and molecules may be obtained from a non-empirical modified electron-gas density functional [6,7]. It is not clear, however, if a simple method like this is appropriate for the description of relatively small effects such as core–valence correlation. We deal with this question, too, in this letter, again for the Li atom.

It is perhaps surprising that so few authors have published distribution functions for correlated atomic densities; the paper by Gupta and Boyd [8] is to our knowledge the first systematic contribution in this field. Their densities for Li and Li^+ are derived from the wavefunction of Weiss [9]. We use these densities as a reference in this letter, together with MRD CI results of Römelt and Peyerimhoff [10].

2. Methods

2.1. Pseudopotentials

Our pseudopotentials for the Li atom are semilocal and contain a projection operator P_0 for the angular quantum number $l = 0$. They are adjusted to valence ionization energies. The accuracy of the fit is 10^{-5} au for the two lowest states ($n = 2, 3$) with $l = 0$ and $l = 1$ symmetry. The errors for the states with $n \geqslant 4$ are less than 10^{-4} au. (Details of the fitting procedure are given in ref. [6].)

Since only valence states are involved in the adjustment, the potentials are not really fixed in the core region: rather large differences can arise here, e.g. with different types of ansatz. There is no need to worry about that point: the arbitrariness in the core region is a fundamental property of pseudopotentials [11].

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Table 1
Pseudopotential parameters A_{ij} (in au)

i	$j = 1$	$j = 2$	$j = 3$	$j = 4$
0	4.926	6.021	15 112	1.824
1	0.334	0.580	6.548	1.276
2	0.0186	0.0994	0.00330	0.112
3	0.598	1.169	6.826	1.310

A pseudopotential which reproduces SCF calculations can be obtained [12] by fitting the parameters A_{0j} in

$$V_{\mathrm{SCF}}(r) = -r^{-1} + f_0(r)\,, \tag{1}$$

with

$$f_i(r) = -A_{i1} r^{-1} \exp(-A_{i2} r^2)$$

$$+ A_{i3} \exp(-A_{i4} r^2)\, P_0\,,$$

to ΔSCF energies (2s: 0.19631, 2p: 0.12840, 3s: 0.07377, 3p: 0.05675 au). The resulting parameter values are given in table 1. A pseudopotential of the same analytic form, which implicitly includes core–valence correlation, is generated [6] by fitting the parameters to experimental ns and np energies (n = 2, 3) [13]:

$$V_1(r) = -r^{-1} + f_1(r) \tag{2}$$

(cf. table 1 for the values of the A_{1j}).

A slightly more refined semi-empirical pseudopotential can be constructed [12] by adding to V_{SCF} one more term which explicitly describes correlation:

$$V_2(r) = V_{\mathrm{SCF}}(r) + f_2(r)\,. \tag{3}$$

The parameters A_{2j} (table 1) are again adjusted to experimental energies for ns, np (n = 2, 3).

Another pseudopotential considered in this work is [2]

$$V_3(r) = V'_{\mathrm{SCF}}(r) + V_{\mathrm{pol}}(r)\,, \tag{4}$$

with

$$V_{\mathrm{pol}}(r) = -(\alpha/2r^4)[1 - \exp(-\gamma r^2)]^2$$

and

$$V'_{\mathrm{SCF}}(r) = -r^{-1} + f_3(r)\,.$$

Here the starting point was the core–polarization potential V_{pol} of Meyer and co-workers [14] (α = 0.1915 au, γ = 0.831 au), which essentially describes core–valence correlation. Then the "SCF" part, V'_{SCF}, of the pseudopotential was readjusted, so that V_3 reproduces the experimental ns, np energies (n = 2, 3) (table 1).

2.2. *Density functional*

In the local spin density (LSD) approximation, corrected for self-interaction [7], the correlation energy E_c is given by

$$E_c = \int (\rho_+ + \rho_-)\, \epsilon_c(\rho_+, \rho_-)\, d\tau$$

$$- \int \rho_+\, \epsilon_c(\rho_+, 0)\, d\tau - \int \rho_-\, \epsilon_c(0, \rho_-)\, d\tau\,. \tag{5}$$

Here ρ_+ and ρ_- are the partial charge densities for spin + and spin −, respectively. The function $\epsilon_c(\rho_+, \rho_-)$ is taken from electron-gas data, in this work we use a recent parameterization by Vosko et al. [15] of correlation energies per particle calculated by Ceperley and Alder [16] for the homogeneous spin-polarized electron gas. Note that the approximation does not contain any parameters adjusted to atomic or molecular properties.

The functional derivative of (5) leads to correlation potentials $\mu_{c\pm}$ for spin + and spin −:

$$\mu_{c\pm} = \mu'_{c\pm}(\rho_+, \rho_-) - \mu'_{c\pm}(\rho_\pm, 0)\,, \tag{6}$$

with

$$\mu'_{c\pm}(\rho_+, \rho_-) = \epsilon_c(\rho_+, \rho_-) - \partial\epsilon_c(\rho_+, \rho_-)/\partial\rho_\pm (\rho_+ + \rho_-)\,.$$

We introduce these potentials into the UHF iteration procedure in the following way: in each iteration step the potentials $\mu_{c\pm}$ are determined for a number of points (80 in our Li and Li^+ calculations); then a least-squares fit is performed with a linear combination of gaussians (16 gaussians with exponents from 0.01 to 2621.44 in this work); the matrix elements of the analytic approximations for $\mu_{c\pm}$ are finally added to the corresponding Fock matrix elements.

2.3. *Basis sets*

In our Li and Li^+ calculations – pseudopotential as well as density functional calculations – we employ the uncontracted 11s gaussian basis set of Huzinaga and Sakai [17]. With this basis set we recover in the LSD calculations 93% of the core–valence correlation energy.

The MRD CI charge densities by Römelt and Peyerimhoff [10], which we use as a reference, were obtained with (11s, 4p, 1d) and (11s, 5p, 2d, 2f) GTO basis sets, the s part being the same as in our calculations. These CI calculations yield 73% and 90%, respectively, of the core–valence correlation energy of the Li atom.

3. Results

As usual, we consider the radial valence electron density

$$D(r) = 4\pi r^2 [\rho_{\mathrm{Li}}(r) - \rho_{\mathrm{Li}^+}(r)] \; . \qquad (7)$$

The densities ρ_{Li}, ρ_{Li^+} are taken from separate calculations for the Li atom and the Li$^+$ ion. (With the pseudopotentials ρ_{Li^+} is set identical zero.)

In order to study the influence of correlation on $D(r)$, we subtract the SCF electron densities from the CI and LSD values, and we subtract the densities with the "SCF" pseudopotentials (V_{SCF}, V'_{SCF}) from those calculated with the corresponding semi-empirical pseudopotentials (V_2, V_3). The area under the $\Delta D(r) \equiv D(r) - D_{\mathrm{SCF}}(r)$ curves thus corresponds to the displacement of electronic charge due to core–valence correlation.

As a measure of the size of the ion and the atom one can use the 0.002 au contours [18]. They are at 3.3 au for Li and at 1.7 au for Li$^+$. The outer maximum of the Li radial density is at 3.1 au.

In fig. 1 we compare our LSD and pseudopotential (V_2) results to the larger of the two MRD CI calculations. One can see that all ΔD curves show the same qualitative behaviour. The effect of core–valence correlation is a charge displacement which renders the Li valence shell less diffuse. The regions where electron charge is withdrawn and where it is accumulated are almost identical in all calculations. The pseudopotential results for the inner core region ($r \leqslant 1$ au) are not shown in fig. 1; the pseudoorbitals are not unique in core region, anyway.

In the valence region, the quantitative agreement between both our pseudopotential and density functional $\Delta D(r)$ and the MRD CI curve is very satisfactory. The deviation is actually smaller than that between dif-

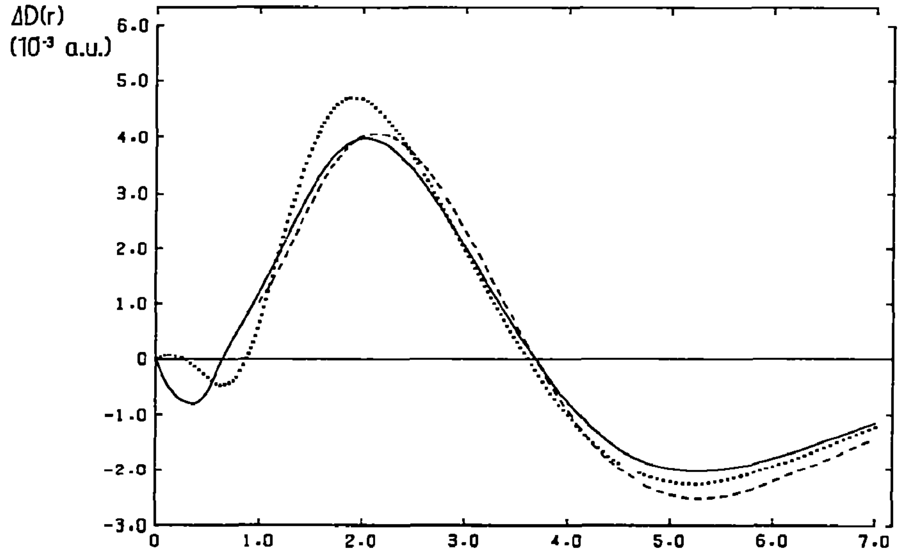

Fig. 1. Valence-electron density differences $\Delta D(r)$ from pseudopotential V_2 (– – –), local spin density functional (...) and MRD CI (——) calculations.

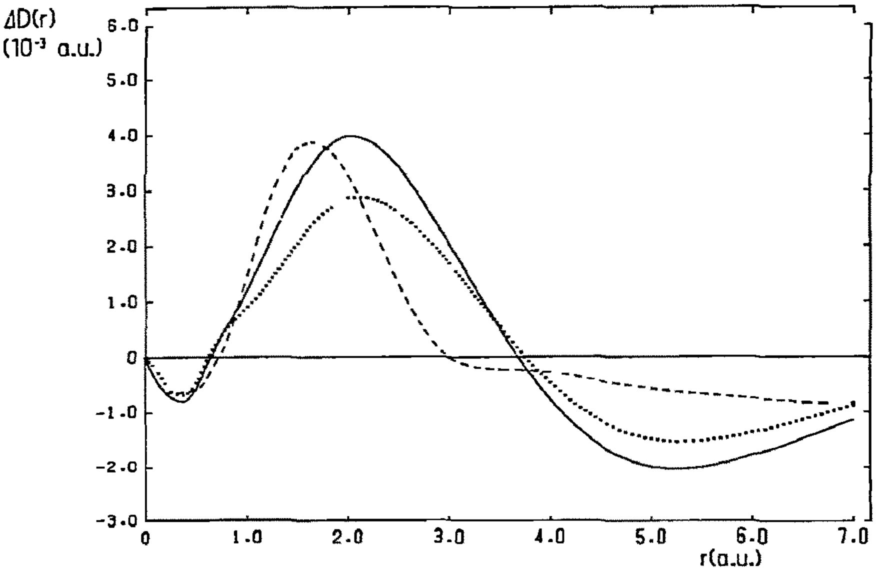

Fig. 2. Valence-electron density differences $\Delta D(r)$ from various CI calculations CI [8,9] (– – –), MRD CI [10] smaller basis (…) and larger basis (——).

ferent CI curves, shown in fig. 2. The basis-set difference between the two MRD CI calculations yields density differences of the order 1×10^{-3} au. The effect is even larger with the Weiss CI wavefunction, this curve is not so suitable, however, for our purpose of comparison, since the SCF and CI basis sets are not the same here.

In fig. 3 we compare the ΔD curves for two differ-

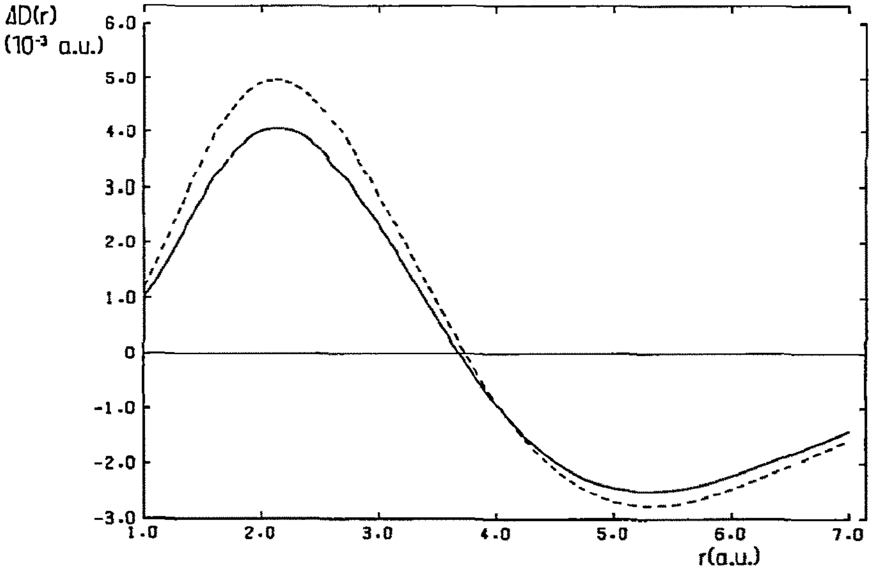

Fig. 3. Valence-electron density differences $\Delta D(r)$ from different pseudopotential calculations: V_2, eq. (3) (——) and V_3, eq. (4) (– – –). The corresponding pseudopotential differences $|V_2 - V_{\mathrm{SCF}}|$ (——), and $|V_3 - V'_{\mathrm{SCF}}|$ (– – –), are given in the lower half (in au logarithmic scale).

ent pseudopotentials (V_2, V_3), in order to check the dependence of our results on the functional form of the pseudopotentials and on the fitting procedure chosen. For illustration, the potentials responsible for the charge displacement ($V_2 - V_{SCF}$, $V_3 - V'_{SCF}$) are also plotted in fig. 3. The potentials are nearly identical in the valence region, as expected. As a consequence of the exponential ansatz, however, $V_2 - V_{SCF}$ decreases too rapidly for large r, but the absolute error is less than 10^{-4} au here. The substantial deviation between the potentials in the core region is not surprising in view of what has been said in section 2.1. The density differences $\Delta D(r)$ in the valence region are comparable to, or even smaller than those which enter through the basis-set dependence in the MRD CI calculations. The V_1 curve, not shown in fig. 3, is quite similar to the V_3 one: the deviation never exceeds 5×10^{-4} au. Another example: a pseudopotential, which was obtained from V_2 by setting $A_{23} = 0$ and readjusting A_{21} and A_{22} to ns energies, yielded $\Delta D(r)$ values virtually identical to those of the original V_2.

Furthermore, we have tested the influence of the basis set on our results. We found that different basis sets of similar quality (e.g. the Huzinaga–Sakai [17] and the van Duijneveldt [19] basis sets) yield valence densities $D(r)$ which may differ by 10^{-3} au. The $\Delta D(r)$ density differences are stable, however, to 3×10^{-4} au in the pseudopotential as well as in the density-functional scheme.

4. Conclusion

It is possible to compute the effect of core–valence correlation on the valence charge density of the Li atom rather accurately by using methods which need only energetic information for atoms (pseudopotentials) or for the homogeneous electron liquid (density functionals). These methods are very simple to use: the computational effort is comparable to that of a SCF calculation; in particular, no polarization functions are needed. In a forthcoming paper, we intend to extend our discussion to heavier alkali atoms (Na, K).

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