THE CORRELATED ELECTRON DENSITY OF ALKALI ATOMS: PSEUDOPOTENTIAL AND DENSITY-FUNCTIONAL RESULTS

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Correlation contributions to the valence-electron densities of the Na and K atoms are evaluated by means of pseudopotential and density-functional methods. The results are compared to ab initio values, and reference is made to previous calculations for Li.

1. Introduction

Core-valence correlation has a rather large effect on the properties of alkali atoms. For the K atom, for example, its contribution to the ionization potential is 0.3 eV(8%) [1,2], and its influence on the dipole polarizability is even more important (the SCF value being too large by 45% [3]). In this letter, we are concerned with changes in valence-electron densities of alkali atoms due to core-valence correlation. We have already presented results for Li in a previous paper (hereafter referred to as I) [4], and now continue that work for Na and K.

Core-valence correlation effects can, in principle, be calculated to any desired degree of accuracy within the framework of configuration-interaction (CI) methods. The computational effort increases rapidly, however, with the number of electrons, and it is difficult to obtain sufficient accuracy. This applies especially to Rb and Cs, where core-valence correlation effects are largest.

We discuss here two alternative approaches:

(i) The density-functional formalism provides a simple means of estimating correlation energies from SCF charge densities and electron-gas data [5]. In its self-consistent version, it is also capable of describing

correlation contributions to charge densities in a reasonable way, as shown in I for Li.

(ii) Pseudopotentials which are fitted to experimental atomic data include core-valence correlation either implicitly [6] or explicitly [7,8] in the form of corepolarization potentials [1,2]. A discussion of correlation effects becomes possible if results are compared with those from SCF-adjusted pseudopotentials [4,9,10].

In section 2 we give a short description of the two approaches, while in section 3 we present our results for Na and K and compare them with ab initio calculations. We conclude with a critical assessment of the merits and shortcomings of the various methods.

2. Methods

2.1. Density functionals

Within the framework of the density-functional formalism, the influence of correlation on charge densities is described by local correlation potentials which are functional derivatives of the correlation part of the density functional. In a local-spin-density (LSD) approximation, corrected for self-interaction [5], the following correlation potentials $\mu_{c\pm}$ (for spin + and

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spin –) are obtained:

$$\mu_{c\pm} = \mu'_{c\pm}(\rho_+, \rho_-) - \mu'_{c\pm}(\rho_\pm, 0) , \qquad (1)$$
with

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

Here, $\epsilon_c(\rho_+, \rho_-)$ is the correlation energy per particle of the homogeneous spin-polarized electron liquid with densities ρ_+ and ρ_- . We use ϵ_c in a parametrized form proposed recently by Vosko et al. [11].

The correlation potentials (1) are introduced into the unrestricted Hartree–Fock (UHF) interation procedure in the way described in I. The number of spherical gaussians used for the analytic representation of the atomic μ_{ct} in our calculations for Na and K is 20.

2.2. Pseudopotentials

We start here with SCF-adjusted pseudopotentials, V_{SCF} , for Na and K which have been shown to be of frozen-core HF quality [12]. As in I, we add to V_{SCF} a correlation potential of the form

$$V_{\rm c} = -(\alpha/2r^4)[1 - \exp(-\beta r^2)]^2 .$$
 (2)

The parameters α and β in V_c are determined by fitting the pseudopotential $V_{ps} \equiv V_{SCF} + V_c$ to experimental ionization energies [13].

In order to study the sensitivity of our results with respect to the fitting procedure chosen, we also test V_c with the parameters α, β used by Müller and Meyer [1] in recent all-electron calculations. (For future reference we call that correlation potential V'_c and the corresponding pseudopotential V'_{ps} .) In V'_c , α is the polarizability of the core and β ensures agreement of the calculated and experimental ionization energies. With this choice, the long-range tail of V'_c is certainly superior to that of the energetically-fitted V_c .

Furthermore, we investigate the influence of the functional form of the correlation potential by changing (2) into

$$V_{\rm c}'' = -a \exp(-br^2), \qquad (3)$$

with parameters a and b adjusted again to experimental ionization energies. The resulting pseudopotential $V_{ps}'' = V_{SCF} + V_c''$ has a long-range behaviour which is distinctly different from that of V_{ps} and V_{ps}' .

Table 1						
Parameters (in a	u) of the	pseudo	potentials	used in	this v	vork

		Na	К
V _{ps}	α	1.205	7.427
	β	0.43	0.18
v'ps	α	0.9947	5.354
	β	0.62	0.29
v _{ps}	a	0.08354	0.12637
	Ь	0.26687	0.14625

The parameters of the pseudopotentials used in this work are compiled in table 1. When fitting to experimental energies, the two lowest s valence ionization potentials were used (3s, 4s for Na; 4s, 5s for K). The accuracy of the fit was 10^{-5} au. If more than one combination of parameters satisfied this criterion, we chose that one which gave the best results for the higher Rydberg terms, as was done in previous work [4,6–9]. With V_c (eq. (2)), the 10^{-5} au criterion for ϵ_{ns} and $\epsilon_{(n+1)s}$ was satisfied for a rather large range of β values (e.g. 0.1 au for K), but, again, the higher Rydberg terms could be used to reduce that interval.

2.3. Ab initio calculations

The ab initio calculations of this work were done by using the method of self-consistent electron pairs (SCEP) [14], which has been extended to use a spinunrestricted open-shell reference determinant [15]. Use is made of the coupled-electron-pairs approximation (CEPA) [16]; CEPA-1 is employed throughout since this version has performed best for properties [3,17].

2.4. Basis sets

In the LSD and pseudopotential calculations of this work, we employ a (14s10p) gaussian basis set contracted to [10s8p] for Na, and a (16s12p) gaussian basis set contracted to [12s9p] for K. We have also performed test calculations with other basis sets, but the density changes were negligible. The basis sets of the CEPA calculations are (14s9p4d)/[12s9p4d] for Na, and (16s10p2d)/[12s8p2d] for K. Volume 100, number 5

3. Results

We present results for valence-electron radial densities, D(r), defined by

$$D(r) = 4\pi r^2 [\rho_X(r) - \rho_{X^+}(r)]$$
, $X = Na, K$. (4)

The densities, ρ_X and ρ_{X^+} , are determined from separate calculations for atoms and ions. With pseudopotentials, ρ_{X^+} has to be put equal to zero, of course.

In order to study the correlation effect on D(r), we subtract UHF densities, $D_{SCF}(r)$, from the correlated results, $D_{corr}(r)$:

$$\Delta D(r) = D_{\rm corr}(r) - D_{\rm SCF}(r) .$$
⁽⁵⁾

With pseudopotentials, the SCF densities are generated from pseudoorbitals determined with V_{SCF} (cf. section 2.2).

The 0.002 au contours of the density ρ are sometimes used to define atomic radii [18]. These contours are at r = 3.3 au for Na and at r = 3.5 au for K. The corresponding values for Na⁺ and K⁺ are 2.4 and 3.1 au, respectively. The maximum of the valence-orbital density is at r = 3.4 au for Na, and at r = 4.4 au for K. In figs. 1 and 2, plots of $\Delta D(r)$ are shown for the two alkali atoms. Our pseudopotential and density-functional results are compared to ab initio CEPA calculations. For Na, two CEPA curves are drawn: for the first, only core-valence correlation has been included, while, for the second, the core has also been correlated. For K, only the first type of CEPA curve is given. With all methods, the same qualitative effect (already described for Li in I) can be observed. D(r) increases in the region where core and valence density overlap. The points which separate the region where charge is withdrawn from that where it is accumulated are nearly the same for all curves.

Let us now discuss the quantitative amount of charge transferred. There is good agreement between the pseudopotential $\Delta D(r)$ and that CEPA calculation which includes core-valence correlation only.

This agreement may be partly fortuitous, however. When all electrons are correlated in the CEPA calculation, the charge transfer is significantly reduced (cf. fig. 1). This is because core correlation reduces the attractive inter-shell correlation, as has been discussed in detail [2]. With our fully correlated CEPA



Fig. 1. Valence-electron density differences $\Delta D(r)$ (in au) for the Na atom from pseudopotential $V_{ps}^{"}$ (-----), LSD (...), and CEPA calculations with (---) and without (---) core correlation.



Fig. 2. Valence-electron density differences $\Delta D(r)$ (in au) for the K atom from pseudopotential $V_{ps}^{"}$ (-----), LSD (...), and CEPA calculations without core correlation (---).

calculations for Na and Na⁺, we recover 80% of the correlation contribution to the experimental ionization energy. The remaining error of 20% may probably be attributed to basis-set deficiencies. Thus, in the basis-set limit, the CEPA $\Delta D(r)$ values could well become larger in magnitude by 20–30%, which would bring them into close agreement with the pseudopotential results.

It should be noted, at this point, that a variational configuration-interaction (CI) wavefunction for intershell and core correlation yields values of $\Delta D(r)$ which are too small if only single and double substitutions are included (CI SD). Unlinked triple substitutions are important here [2]. Without them, $\Delta D(r)$ is smaller in magnitude than the CEPA results by a factor of 2–3 for the Na atom. The effect on the density is considerably larger than the energetic one: the correlation contribution to the ionization energy is 70% with CI SD (versus 80% with CEPA).

In the LSD calculations, which also contain both core-valence and core-correlation contributions, the amount of charge transfer is intermediate between Cl SD and CEPA.

The total correlation energy is well described by LSD (the deviations from the "empirical" values (as quoted in ref. [19]) are only 1% and 5% for Na and

K, respectively) but the correlation contributions to the ionization potentials (IP) are considerably too small (being \approx 45% for Na and \approx 30% for K).

Apparently, energetic effects and density changes exhibit about the same relative errors. For Li, where 93% of the correlation contribution to the ionization energy was recovered in the LSD calculation, the density differences were virtually identical to the pseudopotential ones [4]. We note that, for the group IA and IB elements with atomic number larger than 18, LSD consistently underestimates the correlation contributions to the IPs by a factor of 3 [20]. The LSD $\Delta D(r)$ curves for these atoms are expected, therefore, to be of the same quality as for the K atom.

The question remains: how sensitive are the $\Delta D(r)$ curves to the functional form and the parametrization of the pseudopotential? In figs. 3 and 4, plots of $\Delta D(r)$ are shown for Na and K with the three pseudopotentials V_{ps} , V'_{ps} , and V''_{ps} described in section 2.2. In spite of the rather different long-range behaviour of the correlation part, all three pseudopotentials lead to virtually the same density differences. This is due to the fact that in the physically-important valence region the pseudopotentials exhibit similar behaviour.

Our results are not only insensitive to the choice of the correlation part but also to the choice of the SCF



Fig. 3. Valence-electron density differences $\Delta D(r)$ (in au) for the Na atom from pseudopotential calculations: V_{ps} (...). V'_{ps} (----), V''_{ps} (----).

part of the pseudopotentials. If the correlation potential V'_c is retained, for example, and the pseudopotential as a whole is adjusted to experimental energies [7,8], the density differences are nearly identical to those displayed in figs. 3 and 4. Furthermore, our pseudopotential results compare favourably to allelectron calculations including V'_c [1,2], with the exception of the inner core region of course.

Summarizing, we may state that correlation effects on valence densities are qualitatively similar for Li, Na and K.



Fig. 4. Same as in fig. 3, but for the K atom.

Pseudopotentials are well suited to the determination of the valence density changes due to electron correlation.

In the density-functional calculations, the amount of charge transfer is underestimated for Na and K by about the same factor as is the contribution to the experimental ionization energy.

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References

- W. Müller, J. Hesch and W. Meyer, Communications of the 16th Symposium on Theoretical Chemistry, Wildhaus, Switzerland (1980).
- [2] W. Müller, J. Flesch and W. Meyer, J. Chem. Phys., submitted for publication.
- [3] H.J. Werner and W. Meyer, Phys. Rev. A13 (1976) 13.
- [4] A. Savin, U. Wedig, H. Stoll and H. Preuss, Chem. Phys. Letters 92 (1982) 503: 94 (1983) 536.
- [5] H. Stoll, E. Golka and H. Preuss, Theoret. Chim. Acta 55 (1980) 29.

- [6] H. Preuss, H. Stoll, U. Wedig and Th. Krüger, Intern. J. Quantum Chem. 19 (1981) 113.
- [7] P. Fuentealba, H. Preuss, H. Stoll and L. von Szentpály, Chem. Phys. Letters 89 (1982) 418;
 L. von Szentpály, P. Fuentealba, H. Preuss and H. Stoll, Chem. Phys. Letters 93 (1982) 555.
- [8] P. Fuentealba, J. Phys. B15 (1982) L555;
 P. Fuentealba, L. von Szentpály, H. Stoll, F.X. Fraschio and H. Preuss, J. Mol. Struct. (Theochem) 93 (1983) 213.
- [9] A. Savin, Communications of the 17th Symposium on Theoretical Chemistry, Walberberg, West Germany (1981).
- [10] L.R. Kahn, P. Baybutt and D.G. Truhlar, J. Chem. Phys. 65 (1976) 3826;
 J.C. Barthelat and Ph. Durand, Gazz. Chim. Ital. 108 (1978) 225.
- [11] S.H. Vosko, L. Wilk and M. Nusair, Can. J. Phys. 58 (1980) 1200.
- [12] D. Maynau and J.P. Daudey, Chem. Phys. Letters 81 (1981) 273.
- [13] S. Bashkin and J.O. Stoner Jr., Atomic energy levels and grotrian diagrams, Vol. 1 (North-Holland, Amsterdam, 1975).
- [14] W. Meyer, J. Chem. Phys. 64 (1976) 2901.
- [15] J. Flesch, Thesis, Kaiserslautern (1982);J. Flesch and W. Meyer, to be published.
- [16] W. Meyer, J. Chem. Phys. 58 (1973) 1017.
- [17] W. Meyer, Theoret. Chim. Acta 35 (1974) 277.
- [18] R.F.W. Bader, W.H. Henneker and P.E. Cade, J. Chem.
- Phys. 46 (1967) 3341.
- [19] M.H. Ang, K. Yates, I.G. Csizmadia and R. Daudel, Intern. J. Quantum Chem. 20 (1982) 793.
- [20] A. Savin, P. Schwerdtfeger, H. Preuss, H. Silberbach and H. Stoll, Chem. Phys. Letters, to be published.