Volume 49, number 2 CHEMICAL PHYSICS LETTERS 15 July 1977

THE USE OF PSEUDOPOTENTIALS WITHIN LOCAL-DENSITY FORMALISM CALCULATIONS FOR ATOMS: SOME RESULTS FOR THE FIRST ROW

Sid TOPIOL
Department of Chemistry, Northwestern University,
Evanston, Illinois 60201, USA

Alex ZUNGER
Department of Physics and Materials Research Center, Northwestern University,
Evanston, Illinois 60201, USA

and

M.A. RATNER
Department of Chemistry and Materials Research Center, Northwestern University,
Evanston, Illinois 60201, USA

Received 28 March 1977

The use of a pseudopotential to replace the core electron density within electronic structure calculations of Kohn–Sham type is proposed. An heuristic derivation of such a potential is given. Within the local exchange-correlation scheme, the pseudopotential employed is precisely equivalent to solving a frozen-core problem; this is quite different from the situation encountered in using pseudopotentials in Hartree–Fock calculations, where additional approximations are involved. Numerical results for several excited and ionic states of first row atoms are given; the errors due to the frozen core are less than 10^{-3} hartree.

1. Introduction

The Hartree–Fock (HF) scheme is a widely used and well accepted method for performing electronic structure calculations. Numerous programs exist for performing HF calculations for atoms, molecules and solids. Chemical intuition, along with a vast literature of electronic structure calculations, indicates that most changes in electronic structure occur in what is considered the valence region. Since the time to perform such calculations goes up rapidly as the number of orbitals is increased, one would like to eliminate the core orbitals, thereby reducing the computational time and effort, and stressing the behavior of the valence electrons. Unfortunately, quantum theory tells us that we cannot simply ignore the core orbitals. To remedy this situation, the pseudopotential scheme is often introduced into HF calculations [1–6]. This allows one to replace the core orbitals by an effective potential (pseudopotential). This pseudopotential is designed to have the same effect on the valence electrons as do the core orbitals without explicitly including the core. In practice one usually transforms the valence type basis functions to a smooth, nodeless (generally not core-orthogonal) basis set which can later (after performing the pseudopotential HF calculation) be transformed back to a core-orthogonal set. This introduction of pseudopotentials requires two approximations: the core functions are frozen, and the non-local exchange operator acting on the valence functions is replaced by a local operator.

The local density (LD) approach to electronic structure calculations [7,8] is similar to the HF scheme, except that one replaces the non-local exchange operator of the HF scheme by a local operator which is a functional only of the diagonal density matrix $\rho(\boldsymbol{r},\boldsymbol{r})$ and which, in prinicple, includes all exchange and correlation contributions. One then performs a self-consistent field (SCF) calculation using this local operator. Given this similarity in the HF and LD schemes, it seems likely that the pseudopotential approximation should be helpful in an LD approach. We will show that this in fact proves to be the case. In particular, since the usual HF pseudopotential requires that at one stage in its development we approximate the non-local exchange operators of the core by local operators, and since, in the LD approach, these operators are local to begin with, this part of the approximation (localization of a non-local operator) does not enter. This leaves only the frozen core approximation. One would then expect the pseudopotential approach to be better suited (less of an approximation) to the LD scheme than to HF.

We have presented elsewhere [9] a more detailed development based on the general Kohn–Sham local density formalism. It is the aim of the present note to give an intuitively appealing LD pseudopotential development, and to demonstrate its accuracy for first-row atoms.

2. Development

The LD exchange eigenvalue equation for an atomic orbital with quantum numbers nl is given by

$$H\psi_{nl}(\boldsymbol{r}) = \{\tfrac{1}{2}\nabla^2 + V_\mathrm{T}[\rho(\boldsymbol{r})]\}\psi_{nl}(\boldsymbol{r}) = \epsilon_{nl}\psi_{nl}(\boldsymbol{r})\,, \tag{1}$$

where the total LD potential is:

$$V_\mathrm{T}[\rho(\boldsymbol{r})] = -Z/r + V_\mathrm{coul}[\rho(\boldsymbol{r})] + V_\mathrm{xc}[\rho(\boldsymbol{r})]\,.$$

Here H is the hamiltonian, $\psi_{nl}(\boldsymbol{r})$ is the orbital wavefunction, $-\frac{1}{2}\nabla^2$ is the kinetic energy operator, Z is the atomic number, $V_\mathrm{coul}[\rho(\boldsymbol{r})]$ is the total electronic Coulomb potential, ϵ_{nl} is the orbital energy for $\psi_{nl}(\boldsymbol{r})$ and $V_\mathrm{xc}[\rho(\boldsymbol{r})]$ is given in terms of the charge density $\rho(\boldsymbol{r})$ as:

$$V_\mathrm{xc}[\rho(\boldsymbol{r})] = V_\mathrm{x}[\rho(\boldsymbol{r})] + V_\mathrm{corr}[\rho(\boldsymbol{r})]\,, \quad V_\mathrm{x}[\rho(\boldsymbol{r})] = -3\alpha(3/4\pi)^{1/3}[\rho(\boldsymbol{r})]^{1/3} \tag{2}$$

and $V_\mathrm{corr}[\rho(\boldsymbol{r})]$ is the local correlation operator given by Singwi et al. [10]. The parameter α is taken equal to 2/3. For heuristic purposes, we can for a given valence orbital (unless otherwise indicated, n is assumed to specify the valence shell) divide (1) by $\psi_{nl}(\boldsymbol{r})$ and rewrite it as

$$\epsilon_{nl} = \frac{H\psi_{nl}(\boldsymbol{r})}{\psi_{nl}(\boldsymbol{r})} = -\frac{1}{2}\,\frac{\nabla^2\psi_{nl}(\boldsymbol{r})}{\psi_{nl}(\boldsymbol{r})} - \frac{Z_\mathrm{v}}{r} - \frac{Z_\mathrm{c}}{r} + V^\mathrm{c}_\mathrm{coul}[\rho_\mathrm{c}(\boldsymbol{r})] + V^\mathrm{v}_\mathrm{coul}[\rho_\mathrm{v}(\boldsymbol{r})] + V^\mathrm{v,c}_\mathrm{xc}[\rho_\mathrm{c}(\boldsymbol{r}) + \rho_\mathrm{v}(\boldsymbol{r})]\,, \tag{3}$$

where c and v refer to core and valence respectively. We now define a pseudohamiltonian such that

$$\epsilon^\mathrm{ps}_{nl} = \frac{H_l{}^\mathrm{ps}\psi^\mathrm{ps}_{nl}(\boldsymbol{r})}{\psi^\mathrm{ps}_{nl}(\boldsymbol{r})} = -\frac{1}{2}\,\frac{\nabla^2\psi^\mathrm{ps}_{nl}(\boldsymbol{r})}{\psi^\mathrm{ps}_{nl}(\boldsymbol{r})} - \frac{Z_\mathrm{v}}{r} + V^\mathrm{ps}_\mathrm{coul}[\rho^\mathrm{ps}_\mathrm{v}(\boldsymbol{r})] + V^\mathrm{ps}_\mathrm{xc}[\rho^\mathrm{ps}_\mathrm{v}(\boldsymbol{r})] + V^\mathrm{ps}_l(\boldsymbol{r})\,. \tag{4}$$

Eq. (4) has the form one would expect if only the valence orbitals (or more correctly the pseudoorbitals) were treated explicitly. If we assume some suitably defined pseudoorbital (see section 3), (4) defines our pseudopotential $V_l{}^\mathrm{ps}(\boldsymbol{r})$ in terms of this pseudoorbital $\psi^\mathrm{ps}_{nl}(\boldsymbol{r})$ and $\epsilon^\mathrm{ps}_{nl}$ for the given nl state. Since we wish our pseudohamiltonian to have the same energy spectrum as the original hamiltonian, we set $\epsilon^\mathrm{ps}_{nl} \equiv \epsilon_{nl}$. We then have

$$V_l{}^\mathrm{ps}(\boldsymbol{r}) = \epsilon_{nl} + \tfrac{1}{2}[\nabla^2\psi^\mathrm{ps}_{nl}(\boldsymbol{r})]/\psi^\mathrm{ps}_{nl}(\boldsymbol{r}) + V_0[\rho^\mathrm{ps}_\mathrm{v}(\boldsymbol{r})]\,, \tag{5a}$$

where the l-independent part is:

$$V_0[\rho^\mathrm{ps}_\mathrm{v}(\boldsymbol{r})] = Z_\mathrm{v}/r - V^\mathrm{ps}_\mathrm{coul}[\rho^\mathrm{ps}_\mathrm{v}(\boldsymbol{r})] - V^\mathrm{ps}_\mathrm{xc}[\rho^\mathrm{ps}_\mathrm{v}(\boldsymbol{r})]\,. \tag{5b}$$

Note that since the exchange-correlation term is local to begin with, no localization of this operator is involved in forming this pseudopotential as there would be in the HF pseudopotential scheme. By having set $\epsilon_{nl}^{\mathrm{ps}} = \epsilon_{nl}$, (4) implies that $\psi_{nl}^{\mathrm{ps}}(r)$ is an eigenfunction of $H_l{}^{\mathrm{ps}}$. In other words H_{nl}^{ps} and H_{nl} do not commute. It should be emphasized that in (4) one uses the pseudoorbitals to form the Coulomb and exchange operators. To see this more clearly, as well as the role of the pseudopotential, we subtract (4) from (3) and rearrange to get

$$V_l{}^{\mathrm{ps}}(r) = Z_{\mathrm{c}}/r + V_{\mathrm{coul}}^{\mathrm{c}}[\rho_{\mathrm{c}}(r)] - (\epsilon_{nl} - \epsilon_{nl}^{\mathrm{ps}}) - \frac{1}{2}\left[\frac{\nabla^2\psi_{nl}(r)}{\psi_{nl}(r)} - \frac{\nabla^2\psi_{nl}^{\mathrm{ps}}(r)}{\psi_{nl}^{\mathrm{ps}}(r)}\right]$$

$$+ \{V_{\mathrm{coul}}^{\mathrm{v}}[\rho_{\mathrm{v}}(r)] - V_{\mathrm{coul}}^{\mathrm{ps}}[\rho_{\mathrm{v}}^{\mathrm{ps}}(r)]\} + \{V_{\mathrm{xc}}[\rho_{\mathrm{c}}(r) + \rho_{\mathrm{v}}(r)] - V_{\mathrm{xc}}^{\mathrm{ps}}[\rho_{\mathrm{v}}^{\mathrm{ps}}(r)]\}. \quad (6)$$

Several terms in this equation can be simplified: the third term is zero by definition of our ϵ^{ps}. The fourth and fifth terms are zero for the (nodeless) wavefunctions whose l is greater than any l present in the core. The last term is never $V_{\mathrm{xc}}[\rho_{\mathrm{c}}(r)]$ due to the nonlinearity of the $\rho^{1/3}$term in V_{xc}.

Eq. (5) or (6) serves to define the pseudopotential. For the state used to define the pseudopotential, the treatment is exact. For other states the only approximation (if one orthogonalizes the final pseudoorbitals to the original core orbitals after performing the SCF calculation) [9] is that of a frozen core.

Our pseudoorbital is defined by a linear transformation on the all-electron (exact) orbitals as:

$$\psi_{nl}^{\mathrm{ps}}(r) = \sum_i c_i \psi_{il}(r) . \quad (7)$$

Eq. (7) guarantees that one can regain the original valence orbital by orthogonalizing the pseudoorbital to the core (for the state used to define the pseudoorbital). By choosing the coefficients properly one can eliminate nodes and oscillations in the pseudoorbital; this is required if one is to avoid singularities in the pseudopotential [2,6,9]. In addition such smooth orbitals generally require fewer basis functions to describe them, which results in considerable computational economies. Since (7) mixes an arbitrary amount of core into $\psi_{nl}^{\mathrm{ps}}(r)$ and since one can remove it again (reorthogonalize) after the SCF calculation, this choice is not critical. (For the present work on first row atoms $\psi_{2\mathrm{p}}^{\mathrm{ps}}(r)$ must be identical to $\psi_{2\mathrm{p}}(r)$. For $\psi_{2\mathrm{s}}^{\mathrm{ps}}(r)$ we mix in the minimum amount of $\psi_{1\mathrm{s}}(r)$ required to eliminate the radial node. This is equivalent to the constraint of existing HF algorithms which require [2,6] the coefficients in (7) be chosen such that ψ_{nl}^{ps} go to zero at the origin. For the first row, this condition (along with that of normalization of ψ_{nl}^{ps}) uniquely determines $\psi_{2\mathrm{s}}^{\mathrm{ps}}$.) We can now simplify (5) by recognizing that the orbitals $\psi_{il}(r)$ in (7) are exact eigenfunctions to the all-electron hamiltonian $(-\frac{1}{2}\nabla^2 + V_{\mathrm{T}}[\rho(r)])$ in (1). This would yield:

$$V_l{}^{\mathrm{ps}}(r) = \epsilon_{nl} - \sum_n c_{nl}\psi_{nl}(r)\epsilon_{nl} / \sum_n c_{nl}\psi_{nl}(r) + V_{\mathrm{T}}[\rho(r)] + V_0[\rho_{\mathrm{v}}^{\mathrm{ps}}(r)] . \quad (8)$$

In the particular case of a first row atom this reduces to:

$$V_{\mathrm{s}}^{\mathrm{ps}}(r) = \epsilon_{2\mathrm{s}} - \sum_{i=1\mathrm{s},2\mathrm{s}} c_i\psi_i(r)\epsilon_i / \sum_{i=1\mathrm{s},2\mathrm{s}} c_i\psi_i(r) + V_{\mathrm{T}}[\rho(r)] + V_0[\rho_{\mathrm{v}}^{\mathrm{ps}}(r)] , \quad (9a)$$

$$V_{\mathrm{p}}^{\mathrm{ps}}(r) = V_{\mathrm{T}}[\rho(r)] - V_0[\rho_{\mathrm{v}}^{\mathrm{ps}}(r)] , \quad (9b)$$

$$V_{\mathrm{d}}^{\mathrm{ps}}(r) = V_{\mathrm{f}}^{\mathrm{ps}}(r) = \ldots = V_{\mathrm{p}}^{\mathrm{ps}}(r) . \quad (9c)$$

We now briefly discuss the implications of these equations on the properties of the pseudopotential of the first row atoms. If one were to use the true 2s orbital in (9a), it would have the same form as (9b) (note that $V_0(r)$ would differ numerically) and thus all the l components of the pseudopotential would be the same. It is the process of forming a pseudoorbital for the $l = 0$ wavefunction which causes the $l = 0$ potential to differ from the others. Physically, this effect is a consequence of the Pauli principle felt by electrons whose angular momentum species is present in the core, but not by electrons whose angular momentum species (p, d, f for first row atoms) is absent in the core.

In (9b), the dependence of the p potential on the p orbital enters explicitly through the $V_0(r)$ term where the occupied p orbitals have been used to compute the charge density. Thus if one were to compute, say, the d potential in the same way, using the same original charge density, one would get exactly the same potential for $V_d(r)$ as for $V_p(r)$ (and similarly for all higher angular momenta). Eq. (9c) is thus exact and is a result of the fact that the exchange operator [last term in $V_0(r)$ in (5)] is local in the LD formalism. This is in contrast to the HF based pseudopotentials [2–6] where eq. (9c) is only an approximation which is usually made, on the assumption that the non-local HF exchange operators for valence orbitals of differing l are similar, provided neither l-value is present in the core. In general one can set up equations similar to (9) and generate potentials for l going from zero to one higher than the highest symmetry found in the core ($\equiv l_{\mathrm{core}} + 1$) and set all higher $V_l(r)$ terms to $V_{l_{\mathrm{core}}+1}(r)$.

4. Results

In table 1 we present the results of tests performed with and without the LD pseudopotentials for atoms of the first row. The results for C were given in ref. [9] and are presented here for completeness. It is seen that the errors

Table 1
Comparison of all-electron and pseudopotential calculations (energies in hartrees) a)

Atom	Configuration	Excitation energy b)	Orbital energies c)	
Li	$2s^12p^0$	(−7.174881)	−0.0790	−0.0199
		(−0.165554)	−0.0790	−0.0199
Li	$2s^02p^1$	0.060637	−0.0995	−0.0376
		0.060806	−0.1004	−0.0382
$Li^{1/2+}$	$2s^{1/2}2p^0$	0.061390	−0.1679	−0.0989
		0.061512	−0.1683	−0.0985
Be	$2s^22p^0$	(−14.223291)	−0.1700	−0.0457
		(0.933249)	−0.1700	−0.0457
Be	$2s^12p^1$	0.125781	−0.1931	−0.0660
		0.126108	−0.1950	−0.0673
Be^{1+}	$2s^12p^0$	0.311895	−0.4626	−0.3234
		0.313607	−0.4663	−0.3237
B	$2s^22p^1$	(−24.050406)	−0.3054	−0.1000
		(−2.479522)	−0.3054	−0.1000
B	$2s^12p^0$	0.206252	−0.3239	−0.1168
		0.206411	−0.3259	−0.1185
B^{1+}	$2s^22p^0$	0.264436	−0.6670	−0.4495
		0.263413	−0.6681	−0.4466
C	$2s^22p^2$	(−37.053604)	−0.4574	−0.1580
		(−5.203781)	−0.4574	−0.1580
C	$2s^12p^3$	0.300253	−0.4745	−0.1734
		0.300234	−0.4765	−0.1756
C^{1+}	$2s^22p^1$	0.358022	−0.8900	−0.5799
		0.357367	−0.8924	−0.5782

le 1 (continued)

Atom	Configuration	Excitation energy b)	Orbital energies c)	
N	$2s^2 2p^3$	(−53.567901)	−0.6288	−0.2210
		(−9.441430)	−0.6288	−0.2210
N	$2s^1 2p^4$	0.408783	−0.6458	−0.2360
		0.408594	−0.6478	−0.2385
N^{1+}	$2s^2 2p^2$	0.455262	−1.1301	−0.7122
		0.454785	−1.1333	−0.7109
O	$2s^2 2p^4$	(−73.925421)	−0.8206	−0.2895
		(−15.524905)	−0.8206	−0.2895
O	$2s^1 2p^5$	0.532263	−0.8371	−0.3045
		0.531905	−0.8400	−0.3073
O^{1+}	$2s^2 2p^3$	0.556919	−1.3887	−0.8477
		0.556546	−1.3925	−0.8467
F	$2s^2 2p^5$	(−98.456600)	−1.0330	−0.3635
		(−23.784894)	−1.0330	−0.3635
F	$2s^1 2p^6$	0.670893	−1.0511	−0.3787
		0.670368	−1.0531	−0.3818
F^{1+}	$2s^2 2p^4$	0.663331	−1.6667	−0.9871
		0.663030	−1.6709	−0.9864
Ne	$2s^2 2p^6$	(−127.490729)	−1.2661	−0.4431
		(−34.550852)	−1.2661	−0.4431
Ne^{1+}	$2s^2 2p^5$	0.774660	−1.9643	−1.1308
		0.774412	−1.9689	−1.1302
C	$2s^2 2p^0 3s^2$	0.682987	−0.09435	−0.00935
		0.682886	−0.09422	−0.00934

For each pair of energies the upper value gives the all-electron results.

For the ground state, the total energies are given in parentheses.

The all-electron versus pseudopotential results agree exactly for the state from which the potential was made (the ground states for all results given here).

the orbital energies and excitation energies are less than 10^{-3} au. This is true for excitation energies up to 19 eV, d reflects the error in the frozen core approximation inherent in the pseudopotential scheme; frozen-core LD culations yield precisely the same results as the LD pseudopotential. These calculations all employ numerical itals, so that no basis function inadequacy ever appears. Most of these calculations are for valence-excited states, hough for carbon we present results for highly excited states; these represent a rather stringent test of the neutral und state atom pseudopotential, but even here the results are quite satisfactory. The wavefunctions for N^+ are sented in fig. 1; we show both the nodeless pseudoorbital and the orbital resulting when the pseudoorbital is rehogonalized [11] to the frozen core. Again, the results seem quite good.

These results promise that the LD pseudopotential approach presented here will prove both accurate and useful roviding a method for performing valence-electrons-only LD computations for atoms, molecules and solids. Alugh the present derivation is heuristic, a more rigorous treatment of the same results can be given [9]; the im-

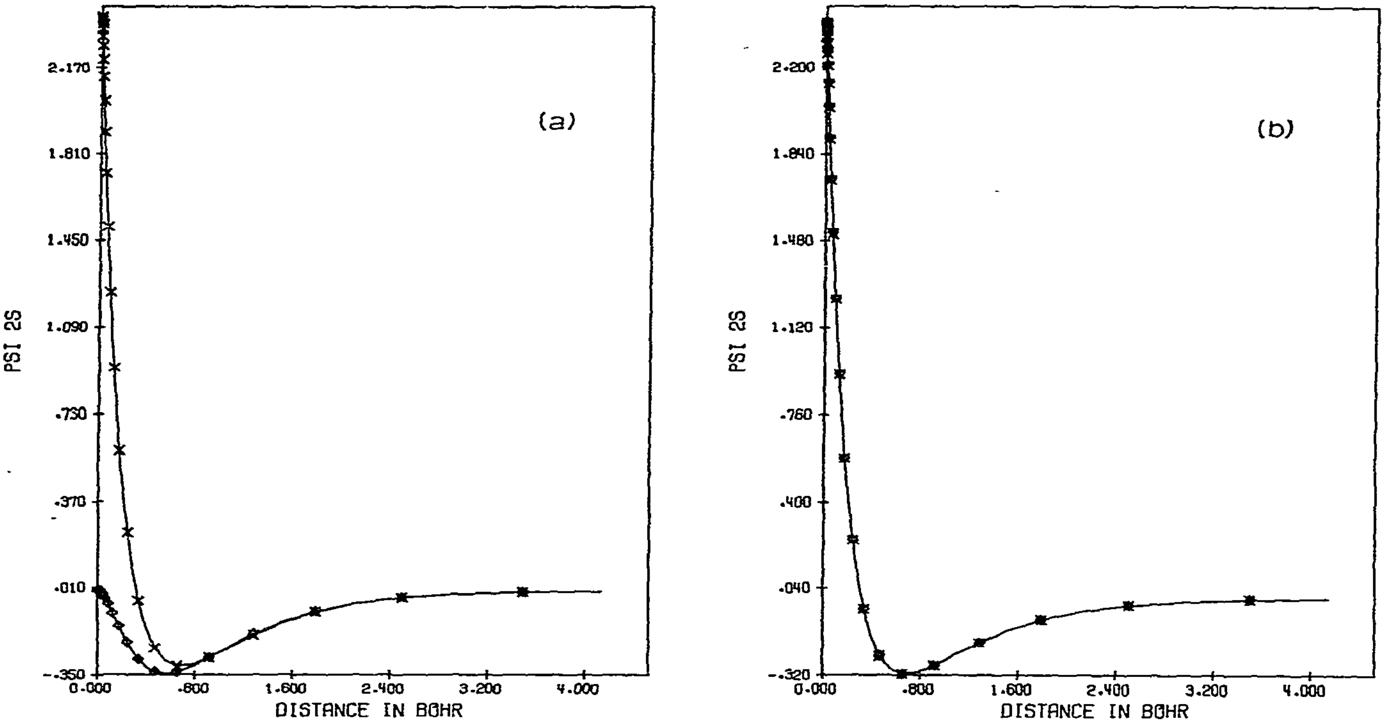

Fig. 1. (a) The actual and pseudo LD 2s orbitals for N^+. X ≡ real 2s, ◇ = pseudo 2s. (b) The actual and core-orthogonalized pseudo 2s orbitals for N^+. X = real 2s, ◇ = pseudo 2s, orthogonalized to frozen (N) core.

portant point is that our LD pseudopotential scheme is exactly equivalent to a frozen-core calculation, and seems highly accurate for the first row results obtained so far*.

Acknowledgement

We are grateful to the NSF for support of this research, partly through the N.U. Materials Research Center. S.T. thanks Jules Moskowitz, Michael Boring and John Wood for useful and incisive comments.

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[*] Snijders and Baerends [12] have very recently proposed a generalized Phillips–Kleinman pseudo potential scheme within the local density formalism. Their method has one distinct advantage over ours with respect to applicability: no projection operators onto angular momentum states need be included. It also has several disadvantages (need to include core density explicitly, non-recovery of frozen-core results).

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