



Just as we replace the non-local exchange operator of the HF scheme by a local operator which is a function only of the diagonal density matrix  $\rho(\mathbf{r}, \mathbf{r})$  and which, in principle, 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 is in fact proven to be the case. In particular, since the usual HF pseudopotential approximation 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. It is where 3operT We have presented elsewhere [9] a more detailed development based on the general Kohn-Sham local density

## 2. Development

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

$$H\psi_{nl}(\mathbf{r}) = \left\{ \frac{1}{2}\nabla^2 + V_T[\rho(\mathbf{r})] \right\} \psi_{nl}(\mathbf{r}) = \epsilon_{nl}\psi_{nl}(\mathbf{r}), \quad (1)$$

where the total LD potential is:

$$V_T[\rho(\mathbf{r})] = -Z/r + V_{\text{coul}}[\rho(\mathbf{r})] + V_{\text{xc}}[\rho(\mathbf{r})].$$

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

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

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

$$\epsilon_{nl} = \frac{H\psi_{nl}(\mathbf{r})}{\psi_{nl}(\mathbf{r})} = -\frac{1}{2} \frac{\nabla^2 \psi_{nl}(\mathbf{r})}{\psi_{nl}(\mathbf{r})} - \frac{Z_v}{r} - \frac{Z_c}{r} + V_{\text{coul}}^c[\rho_c(\mathbf{r})] + V_{\text{coul}}^v[\rho_v(\mathbf{r})] + V_{\text{xc}}^{v,c}[\rho_c(\mathbf{r}) + \rho_v(\mathbf{r})], \quad (3)$$

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

$$\frac{H^{\text{PS}}\psi_{nl}^{\text{PS}}(\mathbf{r})}{\psi_{nl}^{\text{PS}}(\mathbf{r})} = \frac{\nabla^2 \psi_{nl}^{\text{PS}}(\mathbf{r})}{\psi_{nl}^{\text{PS}}(\mathbf{r})} - \frac{Z}{r} + \dots$$

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  $V_l^{\text{PS}}(\mathbf{r})$  in terms of this pseudoorbital  $\psi_{nl}^{\text{PS}}(\mathbf{r})$  and  $\epsilon_{nl}^{\text{PS}}$  for the given  $nl$  state. Since we wish our pseudohamiltonian to be the same as the original hamiltonian, we set  $\epsilon^{\text{PS}} = \epsilon$ . We then have

$$V_l^{\text{PS}}(\mathbf{r}) = \epsilon_{nl} + \frac{1}{2} \left[ \frac{\nabla^2 \psi_{nl}^{\text{PS}}(\mathbf{r})}{\psi_{nl}^{\text{PS}}(\mathbf{r})} + V_0[\rho_v^{\text{PS}}(\mathbf{r})] \right], \quad (5a)$$

where the  $l$ -independent part is:

$$V_0[\rho_v^{\text{PS}}(\mathbf{r})] = Z_v/r - V_{\text{coul}}^{\text{PS}}[\rho_v^{\text{PS}}(\mathbf{r})] - V_{\text{xc}}^{\text{PS}}[\rho_v^{\text{PS}}(\mathbf{r})]. \quad (5b)$$

Note that since the exchange-correlation term is local to begin with, no localization of this operator is involved in

sized 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

$$V_l^{\text{PS}}(r) = Z_c/r + V_{\text{coul}}^c[\rho_c(r)] - (\epsilon_{nl} - \epsilon_{nl}^{\text{PS}}) - \frac{1}{2} \left[ \frac{\nabla^2 \psi_{nl}(r)}{\psi_{nl}(r)} - \frac{\nabla^2 \psi_{nl}^{\text{PS}}(r)}{\psi_{nl}^{\text{PS}}(r)} \right] + \{V_{\text{coul}}^v[\rho_v(r)] - V_{\text{coul}}^{\text{PS}}[\rho_v^{\text{PS}}(r)]\} + \{V_{\text{xc}}[\rho_c(r) + \rho_v(r)] - V_{\text{xc}}^{\text{PS}}[\rho_v^{\text{PS}}(r)]\}. \quad (6)$$

Several terms in this equation can be simplified; the third term is gone by definition of our  $\epsilon_{nl}^{\text{PS}}$ . 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  $V_{\text{xc}}[\rho_c(r)]$  due to the nonlinearity of the  $\rho^{1/3}$  term in  $V_{\text{xc}}$ .

inal 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:

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

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  $\psi_{nl}^{\text{PS}}(r)$  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

chosen such that  $\psi_{nl}^{\text{PS}}$  go to zero at the origin. For the first row, this condition (along with that of normalization of  $\psi_{nl}^{\text{PS}}$ ) uniquely determines  $\psi_{nl}^{\text{PS}}$ .) We can now simplify (5) by recognizing that the orbitals  $\psi_{il}(r)$  in (7) are exact eigenfunctions to the all-electron hamiltonian  $(-\frac{1}{2}\nabla^2 + V_{\text{T}}[\rho(r)])$  in (1). This would yield:

$$V_l^{\text{PS}}(r) = \epsilon_{nl} - \sum_n c_{nl} \psi_{nl}(r) \epsilon_{nl} / \sum_n c_{nl} \psi_{nl}(r) + V_{\text{T}}[\rho(r)] + V_0[\rho_v^{\text{PS}}(r)]. \quad (8)$$

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

$$V_s^{\text{PS}}(r) = \epsilon_{2s} - \sum_{i=1s,2s} c_i \psi_i(r) \epsilon_i / \sum_{i=1s,2s} c_i \psi_i(r) + V_{\text{T}}[\rho(r)] + V_0[\rho_v^{\text{PS}}(r)], \quad (9a)$$

$$V_p^{\text{PS}}(r) = V_{\text{T}}[\rho(r)] - V_0[\rho_v^{\text{PS}}(r)], \quad (9b)$$

$$V_d^{\text{PS}}(r) = V_f^{\text{PS}}(r) = \dots = V_p^{\text{PS}}(r). \quad (9c)$$

differ numerically) and thus all the  $l$  components of the pseudopotential would be the same. It is the process of

... 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  $n$  potential on the  $n$  orbital enters explicitly through the  $V_n(r)$  term where the

... exchange operators for various orbitals of the same angular momentum species. In general one can set up equations similar to (9) and generate potentials for  $L$  values from zero to one high

#### 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)<sup>a)</sup>

Atom	Configuration	Excitation energy <sup>b)</sup>	Orbital energies <sup>c)</sup>	
Li	$2s^1 2p^0$	(-7.174881)	-0.0790	-0.0199
		(-0.165554)	-0.0790	-0.0199
Li	$2s^2 2p$	0.060657	-0.0995	-0.0576
		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	$2s^2 2p^0$	(-14.223291)	-0.1700	-0.0457
		(0.933249)	-0.1700	-0.0457
Be	$2s^1 2p^1$	0.125781	-0.1931	-0.0660
		0.126108	-0.1950	-0.0673
$Be^{1+}$	$2s^1 2p^0$	0.311895	-0.4626	-0.3234
		0.313607	-0.4663	-0.3237
B	$2s^2 2p^1$	(-24.050406)	-0.3054	-0.1000
		(-2.479522)	-0.3054	-0.1000
B	$2s^1 2p^0$	0.206252	-0.3239	-0.1168
		0.206411	-0.3259	-0.1185
$B^{1+}$	$2s^2 2p^0$	0.264436	-0.6670	-0.4495
		0.263413	-0.6681	-0.4466
C	$2s^2 2p^2$	(-37.053604)	-0.4574	-0.1580
		(-5.203781)	-0.4574	-0.1580
$C^{1+}$	$2s^2 2p^1$	0.300234	-0.4765	-0.1756
		0.359367	-0.8904	-0.5799

Table 1 (continued)

energy (eV)

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 <sup>+</sup>	$2s^2 2p^2$	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 <sup>1+</sup>	$2s^2 2p^3$	0.556919	-1.3887	-0.8477
F	$2s^2 2p^5$	(-98.436600)	-1.0550	-0.3633
		(-23.784894)	-1.0330	-0.3635
F	$2s^1 2p^6$	0.670893	-1.0511	-0.3787
		0.670368	-1.0531	-0.3818
F <sup>1+</sup>	$2s^2 2p^4$	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 <sup>1+</sup>	$2s^2 2p^5$	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 all results given here).

the orbital energies and excitation energies are less than  $10^{-3}$  au. This is true for excitation energies up to 10 auV,

orbitals, so that no basis function inadequacy ever appears. Most of these calculations are for valence-excited states, though for carbon we present results for highly excited states; these represent a rather stringent test of the neutral ground state atom pseudopotential, but even here the results are quite satisfactory. The wavefunctions for N<sup>+</sup> are orthogonalized [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

providing a method for performing valence-electron-only LD computations for atoms, molecules and solids. All

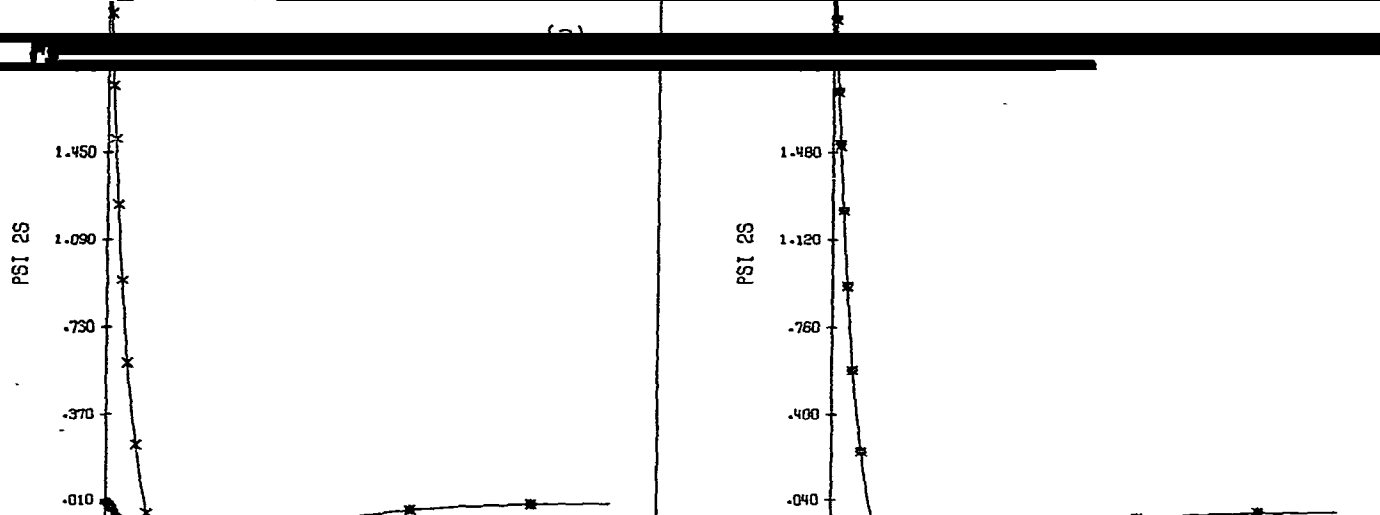


Fig. 1. (a) The actual and pseudo LD 2s orbitals for  $N^+$ .  $\times \equiv$  real 2s,  $\diamond =$  pseudo 2s. (b) The actual and core-orthogonalized pseudo 2s orbitals for  $N^+$ .  $\times =$  real 2s,  $\diamond =$  pseudo 2s, orthogonalized to frozen (N) core.

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

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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 the recovery of frozen-core results).

#### References

- [1] H. Hellmann, Z. Physik 94 (1935) 473.
- [2] C.F. Melius, W.A. Goddard III and L.R. Kahn, J. Chem. Phys. 56 (1972) 3342; L.R. Kahn, P. Baybutt and D.G. Truhlar, J. Chem. Phys 65 (1976) 3826.

- [4] J.C. Barthelat and P. Durand, Chem. Phys. Letters 16 (1972) 63; 27 (1974) 191, and later papers.  
[5] P. Coffey, C.W. Ewig and J.R. van Wazer, J. Am. Chem. Soc. 97 (1975) 1656;  
V. Bonifacic and S. Huzinaga, J. Chem. Phys. 60 (1974) 2779; 62 (1975) 1607;  
M.E. Schwartz and J.D. Switalski, J. Chem. Phys. 57 (1972) 4125;  
G. Simons, J. Chem. Phys. 55 (1971) 756;

S. Tonijal, M.A. Ratner and I.W. Moskowitz, Chem. Phys. Letters 46 (1977) 256;

R. Gaspar, Acta Phys. Acad. Sci. Hung. 3 (1954) 263.

- [11] R.N. Euwema and R.L. Greene, J. Chem. Phys. 62 (1975) 4455.  
[12] J.G. Snijders and J. Baerends, Mol. Phys., to be published.