[redacted] of the diagonal density matrix $\rho(r, r)$ 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. [redacted] at one stage in its development we approximate the non-local exchange operators of the core by local operators, [redacted] 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 [redacted]

2. Development

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

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

where the total LD potential is:

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

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

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

and $V_{\mathrm{corr}}[\rho(r)]$ is the local correlation operator given by Singwi et al. [10]. The parameter α is taken equal to 2/3. [redacted]

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

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

[redacted]

treated explicitly. If we assume some suitably defined pseudoorbital (see section 3), (4) defines our pseudopotential $V_l^{\mathrm{ps}}(r)$ in terms of this pseudoorbital $\psi_{nl}^{\mathrm{ps}}(r)$ and $\epsilon_{nl}^{\mathrm{ps}}$ for the given nl state. Since we wish our pseudohamiltonian [redacted]

where the l-independent part is:

$$V_0[\rho_{\mathrm{v}}^{\mathrm{ps}}(r)] = Z_{\mathrm{v}}/r - V_{\mathrm{coul}}^{\mathrm{ps}}[\rho_{\mathrm{v}}^{\mathrm{ps}}(r)] - V_{\mathrm{xc}}^{\mathrm{ps}}[\rho_{\mathrm{v}}^{\mathrm{ps}}(r)]\,. \quad (5b)$$

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

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

$$+ \{V_{coul}^{v}[\rho_v(r)] - V_{coul}^{ps}[\rho_v^{ps}(r)]\} + \{V_{xc}[\rho_c(r) + \rho_v(r)] - V_{xc}^{ps}[\rho_v^{ps}(r)]\}. \qquad (6)$$

[redacted] fifth terms are zero for the (nodeless) wavefunctions whose l is greater than any l present in the core. The last term is never $V_{xc}[\rho_c(r)]$ due to the nonlinearity of the $\rho^{1/3}$ term in V_{xc}.

[redacted] 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:

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

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 [redacted] computational economies. Since (7) mixes an arbitrary amount of core into $\psi_{nl}^{ps}(r)$ and since one can remove it [redacted] 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 ψ_{nl}^{ps}.) We can now simplify (5) by recognizing that the orbitals $\psi_{il}(r)$ in (7) are exact eigenfunctions to the all-electron hamiltonian $(-\frac{1}{2}\nabla^2 + V_T[\rho(r)])$ in (1). This would yield:

[redacted]

$$V_l^{ps}(r) = \epsilon_{nl} - \sum_n c_{nl}\psi_{nl}(r)\epsilon_{nl} / \sum_n c_{nl}\psi_{nl}(r) + V_T[\rho(r)] + V_0[\rho_v^{ps}(r)]. \qquad (8)$$

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

$$V_s^{ps}(r) = \epsilon_{2s} - \sum_{i=1s,2s} c_i\psi_i(r)\epsilon_i / \sum_{i=1s,2s} c_i\psi_i(r) + V_T[\rho(r)] + V_0[\rho_v^{ps}(r)], \qquad (9a)$$

$$V_p^{ps}(r) = V_T[\rho(r)] - V_0[\rho_v^{ps}(r)], \qquad (9b)$$

$$V_d^{ps}(r) = V_f^{ps}(r) = ... = V_p^{ps}(r). \qquad (9c)$$

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

[redacted] ent 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 $V_p(r)$ term where the [redacted]

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	$2s^1 2p^0$	(−7.174881)	−0.0790	−0.0199
		(−0.165554)	−0.0790	−0.0199
[redacted]				
		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
[redacted]				
		0.300234	−0.4765	−0.1756
C^{1+}	$2s^2 2p^1$	0.358022	−0.8900	−0.5799
		0.357367	−0.8924	−0.5782

ıle 1 (continued)

[redacted]

		energy b)		
[redacted]				
N	$2s^12p^4$	0.408783	−0.6458	−0.2360
		0.408594	−0.6478	−0.2385
N^{1+}	$2s^22p^2$	0.455262	−1.1301	−0.7122
		0.454785	−1.1333	−0.7109
O	$2s^22p^4$	(−73.925421)	−0.8206	−0.2895
		(−15.524905)	−0.8206	−0.2895
O	$2s^12p^5$	0.532263	−0.8371	−0.3045
		0.531905	−0.8400	−0.3073
O^{1+}	$2s^22p^3$	0.556919	−1.3887	−0.8477
[redacted]				
		(−23.784894)	−1.0330	−0.3635
F	$2s^12p^6$	0.670893	−1.0511	−0.3787
		0.670368	−1.0531	−0.3818
F^{1+}	$2s^22p^4$	0.663331	−1.6667	−0.9871
		0.663030	−1.6709	−0.9864
Ne	$2s^22p^6$	(−127.490729)	−1.2661	−0.4431
		(−34.550852)	−1.2661	−0.4431
Ne^{1+}	$2s^22p^5$	0.774660	−1.9643	−1.1308
		0.774412	−1.9689	−1.1302
C	$2s^22p^03s^2$	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.

[redacted]

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 eV,

[redacted]

ıitals, 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 ıund state atom pseudopotential, but even here the results are quite satisfactory. The wavefunctions for N^+ are

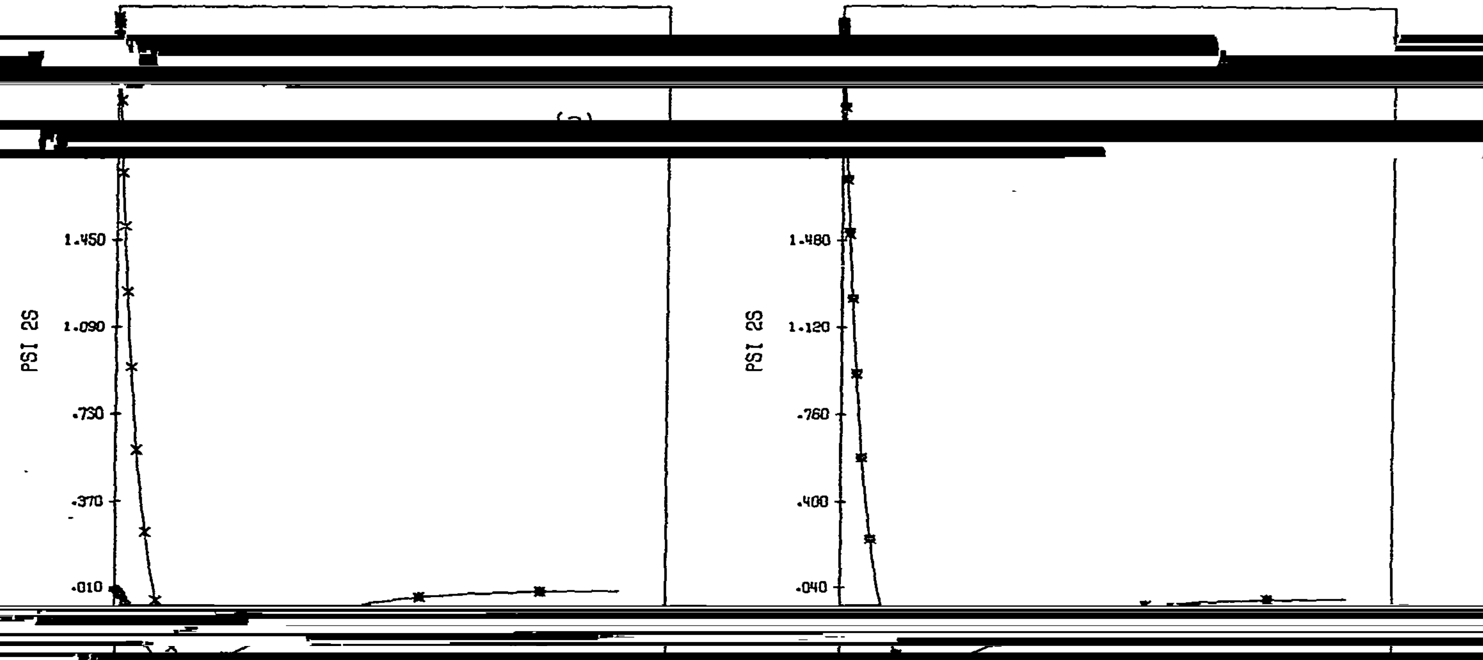
[redacted]

hogonalized [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

[redacted]

[redacted]



[redacted]

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

[redacted]
highly accurate for the first row results obtained so far*.

[redacted]

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S.T. N.O.

* 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).

[redacted]

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