FIRST-PRINCIPLES PSEUDOPOTENTIAL IN THE LOCAL-DENSITY-FUNCTIONAL FORMALISM

and

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A first principles approach to the pseudopotential method is developed in the local density formalism (LDF). As an example, tests on the carbon and tungsten atom potentials are given. Comparison of the energy eigenvalues and total

1. Introduction

The Hartree–Fock (HF) model provides a widely

cal evidence as well as extensive experience with electronic structure calculations indicates that the changes in the first-order density matrices due either to bonding or to low-energy excitations, relative to some standard reference level (e.g. the electronic ground state or the non-interacting atoms limit in a molecule or solid) are mainly brought about by the outer "valence" orbitals while the inner "core-like" orbitals remain largely unchanged. These latter orbitals are not only of little direct interest for many electronic-structure problems, but also necessitate an additional substantial computational effort particu-

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fixed basis set (e.g. linear combination of atomic orbitals or LCAO). Although for many electronic structure problems it is desirable from the computational

all other electrons. To overcome this difficulty the pseudopotential scheme is often introduced [4]. The basic idea is then to remove the constraint of the standard canonical HF theory which requires the valence orbitals to be orthogonal to the core orbitals. This is accomplished by adding to the hamiltonian a term (Phillips–Kleinman pseudopotential [4]), which projects out the core components of a valence type wavefunction. This permits the use of smooth and nodeless valence "pseudo-orbitals" which are usually obtained by a transformation of the atomic HF orbitals. A second term, approximating the coulombic and exchange effects of the missing core electrons (without having explicitly to introduce core orbitals into the problem) is then added and the core electrons are removed. This transformation on the wave-

function is not *unique* since there is an infinite num-

transformation of the HF orbitals that results in pseudo-orbitals having, say, a maximum similarity to the original orbitals, in some preferred parts of space [5-8].

The HF pseudopotential scheme involves three major assumptions: (i) the core orbitals entering the density matrix and the pseudopotential are "frozen" in a given reference electronic state and are taken as such for all excited states as well as for all the different bonding situations (e.g. atoms in molecules and

past [6,9-12] and seems to be useful for evaluating electronic properties that do not sample directly the core region. (ii) Unlike the situation encountered in the all-electron HF model, it is assumed that a radi-

exchange terms exists. This assumption is needed in

behavior of all valence orbitals belonging to the same *l*-value and different excitation states is similar in the core region. (iii) The pseudopotentials for all *l*-states not appearing in the core (or for the next higher *l*

approximation can be relaxed, it appears to be useful

HF calculations have been recently applied to numerous atoms [6] and molecules [7-12] with considerable saving in computational effort.

Parallel with the development of first-principles HF pseudopotentials, substantial effort has been

‡ The elimination of the core orbitals from the electronic

tions are orthogonalized to the core (and hence matrix elements of core basis functions still need to be evaluated), in

orbitals of the all-electron problem are replaced and hence the consideration of core integrals is not necessary.

directed in the past towards the construction of both

model pseudopotential schemes [14-17] which attempt to simulate HF results via model potentials with adjustable parameters. While being useful in practical applications [13-17] both schemes show a

on the basis set used.

The local density functional (LDF) formalism developed by Hohenberg and Kohn [18] and by Kohn and Sham [19] offers a different route to the solution of electronic structure problems in that it

correlation effects in the form of a single-particle potential. It has been widely used in one form or another (including the simplified Hartree-Fock-Slater method) by the vast majority of electronic

studies. The difficulties in having to include the core

including in the local potential a term projecting out explicitly the core orbitals. This enables one to use smooth nodeless valence wavefunctions instead of the original all-electron wavefunctions that have pro-

scheme. In addition to the usual non-uniqueness of the definition of the pseudo-orbitals, this scheme is hard to carry out in practice due to the need to use exact core orbitals (which require a full solution of some related all-electron problem), and the need to recalculate the projection operators for each excited state. More importantly, one is still faced with the

which the various Fourier components of the crystal pseudopotential are used as adjustable parameters

modified to obtain agreement with some observed eigenvalue differences [13].

In this paper we present a first-principles approach
to the pseudopotential problem in the local density

compared to the analogous procedure within the HF

ity of the all-electron potential appearing in the
"standard" LDF formalism (i.e. in which only the
non-gradient electron correlation functionals [19,25]
are included), approximations (ii) and (iii) which are

unnecessary. The resulting pseudopotential is there-
fore exact for the reference state, while for states dif-

tains inaccuracies proportional to the change in the
core contribution to the density matrix. These

problems of interest. For example, the nth moment
of the vector r within the 1s orbital density $\rho_{1s}(r)$ of
carbon: $\int \rho_{1s}(r)r^n dr$ equals in atomic units 64.1056;
5.5995; 0.27303; 0.10104 for $n = -2, -1, 1$ and 2
respectively in the ground $1s^2 2s^2 2p^2$ configuration
and 64.1942; 5.6036; 0.2728; 0.10089 for the
excited $1s^2 2s^1 2p^3$ configuration where all the quanti-
ties are calculated using all-electron LDF. In addition

conceptually more appealing than in the Hartree—
Fock method, due to the suitability of the slowly-
varying-density approximation [19,25,26] used in the
expansion of the total exchange and correlation

smooth and nodeless valence orbitals. As in any pseu-

seeming arbitrariness is, however, less serious than
first appears. We show that although many useful

appear if the pseudo-orbitals are orthogonalized to
the core orbitals *after* the self consistent pseudo
hamiltonian has been solved.

Section 2 is devoted to the derivation of our LDF

properties. Section 3 contains details of the calcula-

applications for both eigenvalues and total energy dif-
ferences as well as wavefunction related properties for

the carbon and tungsten atoms. Section 5 consists of

the density functional approach.

2. Development of the local density pseudopotential

Our development of the local density pseudopo-
tential proceeds as follows: one first solves the local
density $(N_c + N_v)$-electron problem for an atom in

where N_c and N_v denote the number of core and val-

mentum species a rotation of the ground state orbi-
tals is performed such that one obtains new valence

to the core, smooth and nodeless. One then concen-
trates on the variational local density solutions of a
fictitious N_v-electron atom (pseudo-atom) having the
pseudo-orbitals as its eigenvectors and the exact all-
electron-orbital energies as its eigenvalues. Such a
pseudo-atom experiences the Coulomb and exchange-
correlation field of its N_v-electrons plus some yet un-
specified external static potential (which can be dif-

electron eigenvalues, the pseudo-orbitals and the cor-
responding local density potentials. It is then fixed at
its value obtained for the chosen reference electronic
state and applied as such (static core approximation)

pseudo-atom. The properties calculated for the

energies and excited state pseudo-orbitals whose
changes from the ground state pseudo-orbitals match
the changes that the real atomic orbitals would have

these pseudo-orbitals to the ground state core orbi-
tals of the real atom, one would recover the orbitals
for the real atom in the corresponding state subject to
a frozen core approximation.

equation for the electronic states ψ_{nl}^s of an atom with

$$H\psi_{nl}^s(\mathbf{r}) = \{-\tfrac{1}{2}\nabla^2 + V_{tot}[\rho_s(\mathbf{r})]\}\, \psi_{nl}^s(\mathbf{r}) = \epsilon_{nl}^s \psi_{nl}^s(\mathbf{r}) ,$$

(1a)

where the one-body potential is given by:

$$V_{tot}[\rho_s(r)] = -Z/r + V_{Coul}[\rho_s(r)] + V_{xc}[\rho_s(r)] . \quad (1b)$$

Here $V_{Coul}[\rho_s(r)]$ and $V_{xc}[\rho_s(r)]$ are respectively the electronic Coulomb and the exchange- and-correlation local potentials [26] due to the all-electron charge density $\rho_s(r)$, and $\psi_{nl}^s(r)$ and ϵ_{nl}^s denote the central-field (n, l) eigenfunction and eigenvalue, respectively (square brackets denote functional dependence; s is a running index). The Coulomb po-

We now divide the eigenvectors and the charge density into two parts: the "core" part (with eigenvectors $\psi_{nl}^{c,s}(r)$ containing N_c^s electrons) and a "valence" part (with eigenvectors $\psi_{nl}^{v,s}(r)$ and density $n_s^v(r)$ with N_v^s electrons). We will denote *all-electron* (core + valence) densities by $\rho(r)$ and *valence* pseudo-densities by $n(r)$. By valence electrons we mean those given by the aufbau principle as outside a rare gas core (2s, 2p for row 1, 3s, 3p for row 2, 4s, 4p, 3d for row 3, etc.). It would hence suffice for our pur-

$$V_{Coul}[\rho_s(r)] = \int \frac{}{|r-r'|} \quad (2)$$

system (including the self-interaction term). The exchange and correlation potential is given to the

on the relative insensitivity of the bonding character-istics to dynamic electron–electron interactions in the above-defined core; it does not imply any distinguishability between core and valence electrons. A generalization of our formalism to a more flexible definition of core is straightforward but will not concern us here. (Such a generalization is presented in ref. [28].) Since we will be interested in a smooth and nodeless representation for the valence orbitals $\psi_{nl}^{v,s}(r)$, we generate these by relaxing the orthogonality constraint to the core orbitals. Concentrating on a chosen reference electronic state e of the atom, we generate the smooth orbitals for this state by a deorthogonalization procedure, namely:

$$V_{xc}[\rho_s(r)] = V_x[\rho_s(r)] + V_c[\rho_s(r)] , \quad (3)$$

where $V_x[\rho_s(r)]$ is the well known [19,25] "$\rho^{1/3}$" term:

$$V_x[\rho_s(r)] = -(3/\pi)^{1/3} [\rho_s(r)]^{1/3} \quad (4)$$

and $V_c[\rho_s(r)]$ is likewise a local function of r, which was worked out by several authors [26,27] in numerical form and given by Hedin and Lundqvist [25] in an analytically fitted form. The total charge density is related to the eigenvectors of all the σ_{oc} occupied states by:

$$\rho_s(r) = \sum_{nl}^{\sigma_{oc}} N_{nl}^s \psi_{nl}^{s*}(r) \psi_{nl}^s(r) , \quad (5)$$

where N_{nl}^s are the occupation numbers for the electronic configuration s. Eq. (1) is solved self-consis-

$$\varphi_{nl}^{v,e}(r) = C_{nl,nl}^e \psi_{nl}^{v,e}(r) + \sum_{n'l \neq nl}^{core} C_{nl,n'l}^e \psi_{n'l}^{c,e}(r)$$

or

$$\varphi_{nl}^{v,e}(r) = \sum_{n'l} C_{n'l,nl}^e \psi_{n'l}^e(r) , \quad (6)$$

where $\psi_{n'l}^e(r)$ stands for both core and valence orbi-

density matrix [eq. (5)]. Since only the total wavefunction [and not the individual orbitals $\psi_{nl}^s(r)$ of eq. (1)] is invariant under point-group rotation, the orbitals themselves are not determined uniquely by that equation and hence one usually requires orthogonality between them. This results in the familar nodal behavior of the higher eigenfunctions (due to

$\varphi_{nl}^{v,e}(r)$ is normalized and nodeless. This would leave (for an atom belonging to the second or higher rows in the periodic table) some unused degree of freedom in constructing $C_{nl,n'l}^e$. (See ref. [28] for details.)

We will now be interested in the local-density variational problem for a "pseudo-atom" having only N^e electrons arranged in the electronic configuration

of basis functions to adequately describe them in LCAO type expansion models.

tals $\{\varphi_{nl}^{v,e}(r)\}$. To obtain the N_v-electron one-body potential that would yield such variational solutions we

consider first the local-density total energy E_t of such an electronic system subject to the Coulomb and exchange-correlation interactions among its N_v-electrons plus an additional static *external field* $V_{ext}^e(r) = -N_v/r + V_l^e(r)$:

$$E_t = \int n_e(r) V_{ext}^e(r) \, dr + \tfrac{1}{2} \int n_e(r) V_{Coul}[n_e(r)] \, dr$$

where $n_e(r)$ is the variational density for the system in state e and $T_0[n_e(r)]$ is the non-interacting kinetic energy of the electron system with density $n_e(r)$. $E_{xc}[n_e(r)]$ is the total exchange and correlation energy of the interacting N_v^e-electron system. For suf-

$$E_{xc}[n_e(r)] = \int n_e(r) \, \epsilon_{xc}[n_e(r)] \, dr , \qquad (8)$$

on E_t with respect to the density $n_e(r)$ and replaces the functional derivative of the non-interacting kinetic energy $T_0[n_e(r)]$ with respect to $n_e(r)$ by the

$$\{-\tfrac{1}{2}\nabla^2 + V_{eff}(r)\} \, \varphi_{nl}^{v,e}(r) = \lambda_{nl}^{v,e} \varphi_{nl}^{v,e}(r) , \qquad (9)$$

where

$$V_{eff}^e(r) = -N_v/r + V_l^e(r) + V_{Coul}[n_e(r)] + V_{xc}[n_e(r)] ,$$

and the exchange and correlation potential is given by:

$$V_{xc}[n_e(r)] = d(n_e(r) \, \epsilon_{xc}[n_e(r)])/dn_e(r) \qquad (10)$$

$$n_e(r) = \sum_{nl}^{occ} N_{nl}^e |\varphi_{nl}^{v,e}(r)|^2 . \qquad (11)$$

states that are not present in the core of the real atom

(9) with the density given in (11) is now used to *define* the external potential $-N_v/r + V_l^e(r)$ in terms of the eigenvalues $\{\lambda_{nl}^{v,e}\}$ and eigenvectors $\{\varphi_{nl}^{v,e}\}$. We require that the pseudo-hamiltonian in eq. (9):

$$H_l^{PS}\varphi_{nl}^{v,e}(r) = \lambda_{nl}^{v,e}\varphi_{nl}^{v,e}(r) \qquad (12)$$

$\lambda_{nl} - \epsilon_{nl}$). Hence for a single chosen reference state e, it is possible to define an external potential:

$$V_{ext}^e(r) = -N_v/r + V_l^e(r) = \epsilon_{nl}^e + \tfrac{1}{2}\nabla^2\varphi_{nl}^{v,e}(r)/\varphi_{nl}^{v,e}(r)$$
$$- V_{Coul}[n_e(r)] - V_{xc}[n_e(r)] , \qquad (13)$$

atom would yield via the self-consistent solution of

niently by using the fact that $\psi_{nl}^e(r)$ are solutions to the all-electron hamiltonian $-\tfrac{1}{2}\nabla^2 + V_{tot}[\rho(r)]$ [eq. (1)], yielding

$$\sum_{n'l'} C_{nl,n'l'}^e \psi_{n'l'}^e(r)$$

$$+ \{V_{tot}[\rho_e(r)] - V_{tot}[n_e(r)]\} , \qquad (14)$$

where $V_{tot}[\rho_e(r)]$ is the total potential of the all-electron density $\rho_e(r)$ [eq. (1)] and $V_{tot}[n_e(r)]$ is the corresponding total potential of the pseudo (valence)

of basis functions in its LCAO solution on account of the nodeless character of its occupied orbitals.

Obviously, this simplification by itself does not

construction of $V_l^e(r)$ for this state. However, to the

by an *external* potential (which replaces these effects

state, such a pseudopotential transformation becomes

potential $V_{ext}^{e}(r)$ defined for some reference state e, replaces the dynamic core effects for any electronic arrangement of the valence electrons. The pseudopo-

ues ϵ_{nl}^{e}, eigenvectors $\psi_{nl}^{e}(r)$, the total potential $V_{tot}[\rho(r)]$ and expansion coefficients $\{C_{nl,n'l}^{e}\}$. This fixes $V_i(r)$ at the reference state e and from this point on $V_i(r)$ is treated as a static external field acting on the electrons of the pseudo-atom via eq. (9) for any arbitrary electronic state $s \neq e$. In the general case, the eigenvalues ϵ_{nl}^{s} and the total energy [eq. (6)] dif-

states i and j) would not equal exactly those obtained from the all-electron problem [eq. (1)] (H_l^{PS} in (12) does not commute with the all-electron hamiltonian in (1a)). The usefulness of our present approach hence depends entirely on the question of whether our static external potential $V_i(r)$ is capable of simulating the dynamic effects of the core electrons *for any arbitrary electronic state of the atom or the atom placed in a bonding environment* (e.g. the validity of our static core approximation). This can be tested by solving both (1) and (9) self-consistently for a series of states, using for the latter a *fixed* pseudopotential generated, say, from the ground state. We will show in the next section by means of particular

tained in solving (9) with the pseudopotential (14), hence confirming the insensitivity of the valence field to the small core changes attendant on such proces-

exactly equivalent to the "frozen-core" approximation common in quantum-chemical electronic structure calculations in that the results obtained with the

method over the frozen-core approach is that with

lence of the presently developed static core approximation to the frozen-core approximation does not

in the latter scheme additional approximations to the all-electron problem are necessary (see introduction) to reduce the all-electron problem into a pseudopo-

valence field in the HF scheme, while in the local density model the diagonal first-order density matrix determines the potential field uniquely.

It is obvious from eq. (14) that the effective potential in the pseudo-atom $V_{eff}(r)$ is weaker than the full core + valence potential in the real atom $V_{tot}[\rho_e(r)]$ due to the cancellation with the first two terms on the rhs of eq. (14). This is a manifestation of the "Phillips cancellation theorem" [4] and is brought about by the balancing of the attractive Coulomb singularity that a valence electron feels in the core region and the repulsive kinetic terms arising from the nodal behavior of the all-electron valence orbitals. It is noted that for valence orbitals that do not have a matching l-counterpart in the core orbitals (and are therefore nodeless), the sum in the second term in (14) reduces to one term (over the nodeless valence orbital only) and hence cancels with the first term, leaving a relatively "strong" external potential. Hence, while the "s" total effective potential in first-row atoms is relatively weak and can be treated perturbationally in solid-state pseudopotential calculations [12] (the terms strong and weak used apply for radial distances larger than 1.5 bohr) the p and d total effective potentials are not amenable to such treatments and indeed give rise to serious convergence dif-

tential differs distinctly from many other pseudopotential schemes [30–32] in that in the latter case atoms with more than one valence electron are not

core-valence type effects. (The core of, say, an O^{5+} ion is not very much like that of the O atom.) Similar advantages are enjoyed by the Hartree–Fock potentials which have been constructed by an analogous procedure [5–8].

We may briefly discuss some properties of the pseudopotential in eq. (14). When one considers the lowest nodeless valence orbitals in an atom (e.g. 2p, 3d) the transformation in (6) is trivial since no core orbitals have to be mixed into the valence orbitals to produce a nodeless functions and hence $\varphi_{nl}^{v,s}(r) \equiv$

match the real atom valence orbitals $\psi_{nl}^{v,s}(r)$ in the region of space considered relevant for the observable of interest. This approach has led to many prescriptions in HF pseudopotential schemes and leads to acceptable but approximate results. In this approach the expectation value of an operator $\hat{O}$ is usually calculated directly from the pseudo-charge density:

$$n^v(r) = \overset{\text{valence}}{\underset{nl}{\sum}} N_{nl}|\varphi_{nl}^v(r)|^2 , \tag{17}$$

$$V_L^e(r) = V_{\text{tot}}[\rho_e(r)] - V_{\text{tot}}[n_e(r)] . \tag{15}$$

Hence, for a first row-atom only $l = 0$ and $l = 1$ pseudopotentials have to be computed since V_2 equals exactly V_1, etc. This is distinctly different from the situation encountered in the HF pseudopotential theory [8] in which, due to the non-locality of the exchange, V_2 is only approximately equal to V_1. (Similarly, if one is to use the exact all-electron orbital $\psi_{nl}^e(r)$ in eq. (14) instead of the pseudo-orbital (eq. (6)) the pseudopotential would reduce to the form (15) for all l-components.) Hence, when the pseudopotential is used in molecular or solid-state calculations in the form:

$$\infty$$

$$n^c(r) = \overset{\text{core}}{\underset{nl}{\sum}} N_{nl}\psi_{nl}^{c*}(r) \, \psi_{nl}^c(r) \tag{18}$$

to yield:

$$\langle \hat{O} \rangle = \int \{n^c(r) + n^v(r)\} \, \hat{O} \, dr , \tag{19}$$

with the expectation value over a valence pseudo-orbital is given by:

$$\langle \hat{O} \rangle_{nl} = \int \varphi_{nl}^{v*}(r) \, \hat{O} \varphi_{nl}^v(r) \, dr . \tag{20}$$

We will illustrate in the next section some numerical results obtained with this "maximum similarity" approach (b). Alternatively, one can use for the atom any convenient choice of $\{C_{nl,n'l}^e\}$ (obtaining in each case the exact reference state valence eigenvalues) e.g.

where l_A and m_{l_A} define the spherical harmonics on site A, only the lowest members need to be calculated

pseudo-orbital expansion coefficients $C_{nl,n'l}^e$ in eq. (6)

orbital. Any choice of these coefficients that fulfils the above requirements should yield, for the refer-

the all-electron local-density hamiltonian. If, however, it is desired that expectation values (other than orbital energies) over the pseudo-orbitals match closely those yielded by the exact all-electron valence

the coefficients $\{C_{nl,n'l}^e\}$ so that $\varphi_{nl}^{v,e}(r)$ would closely

solved, one orthogonalizes the pseudo-orbitals to the core orbitals of the real atom. This yields orthogalized pseudo-orbitals $\tilde{\varphi}_{nl}^v(r)$ given by:

$$\varphi_{nl}(r) = \left[\varphi_{nl}(r) - \underset{nl}{\sum} \langle \varphi_{nl}(r)|\varphi_{nl}^v(r)\rangle \psi_{nl}^v(r) \right] A , $$

where A is the normalization constant, and the

$$\tilde{n}^v(r) = \overset{\text{valence}}{\underset{nl}{\sum}} N_{nl}|\tilde{\varphi}_{nl}^v(r)|^2 . \tag{22}$$

In this case, expectation values are taken directly on $\tilde{\varphi}_{nl}^v(r)$. If the pseudo-orbitals $\varphi_{nl}^v(r)$ are found for the

$n^v(r) + n^c(r)$, while if the equation is solved for a *different excited state* or for a polyatomic system, the

gonalization procedure in (21) is easy and straightforward to perform since the major time-saving step has already been utilized in solving a simplified self-consistent local density equation for the valence electrons only.

3. Details of calculation

The calculations required here contain two essen-

dopotential by solving the pseudo one-particle equation (9) for arbitrary electronic states and using the

local density equation [eq. (1) with the functionals defined in (2)–(5) for a chosen reference state. It has been customary in the HF pseudopotential approaches [5–7] to carry out this step (as well as to test the pseudopotential) by expanding the solution $\psi_{nl}^S(r)$ in (1) or $\varphi_{n,l}^S(r)$ in (6) in a fixed basis set (e.g. gaussians) and similarly to represent the pseudopotential by some analytical fit. Although this procedure is usually satisfactory [5–8], it represents an unnecessary approximation for the atomic problem. We avoid these approximations by employing a direct numerical technique with no basis set expansions. We use a standard predictor–corrector method [33] in an inwards–outwards integration scheme. The numerical accuracy in the eigenvalues is 10^{-8} au. The total energy is calculated from (7) by using the charge density matrix constructed from the eigenvalue problem, to yield

$$E_t = \sum_i^{occ} \epsilon_i - \tfrac{1}{2} \int\int \frac{\rho(r)\,\rho(r')}{|r - r'|}\, dr\, dr'$$

$$+ \int \rho(r)\{\epsilon_{xc}[\rho(r)] - V_{xc}[\rho(r)]\}\, dr,\qquad (23)$$

E_t is the total energy for the all-electron and for the valence-electron cases, respectively. The sum in the

(23) are calculated by direct numerical integration. The accuracy in evaluating the total energy in eq. (23) is 10^{-7} au.

We chose here as a reference state for the atom the ground electronic state (although, as demonstrated in the next section, a similar accuracy in the predictions

obtained with other choices too). Having solved eq. (1) for this state, the eigenvalues $\epsilon_{n'l'}^e$, the eigenfunctions $\psi_{n'l'}^e(r)$ and the total self-consistent potential

cally from the pseudo-orbitals. In step (b) we use these pseudopotentials to solve eq. (9) for a series of

lated from eqs. (17) and (18) and the orthogonality coefficients required in eqs. (21) and (22) are computed numerically.

The operators $\hat{O}$ [eqs. (19) and (20)] chosen for testing the resulting pseudo wavefunctions are r^n with $-2 < n \leqslant +3$ for the orbital expectation values, and $\exp(iq \cdot r)$ for the charge density expectation values. The latter quantity (atomic X-ray scattering factor) is calculated for a series of momentum values q from the standard form for the central field given by

$$f(q) = \int \frac{\sin(q \cdot r)}{q \cdot r} \rho(r)\, dr,\qquad (24)$$

where $\rho(r)$ can be: (a) the all-electron density, (b) the pseudo-charge density plus frozen core density or (c) the orthogonalized pseudo-charge density plus frozen core density.

4. Illustrative results; carbon and tungsten atoms

4.1. The pseudopotential

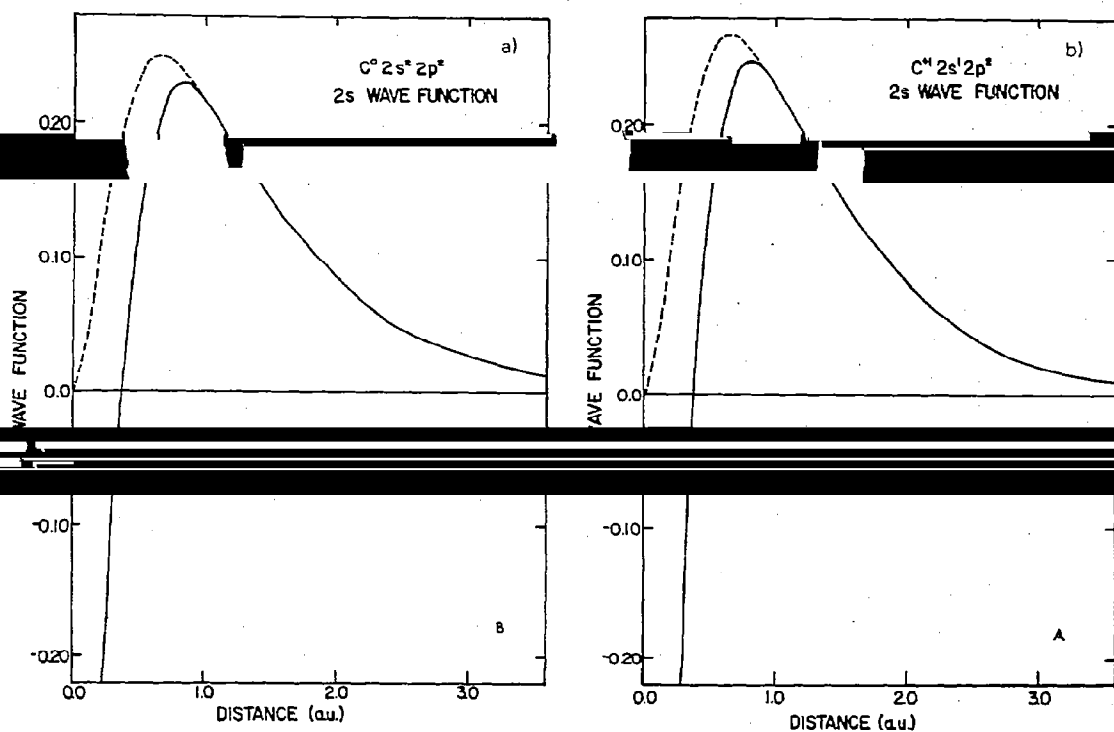We generate the pseudopotential $V_s(r)$ and $V_p(r)$

Fig. 1. All-electron (———) and pseudo (– – –) 2s wavefunctions for: (a) the s^2p^2 ground state of carbon atom. (b) the ionized state.

[34]. The exact $\psi_{2s}^g(r)$ orbital obtained from the solution of (1) is depicted in fig. 1a together with the pseudo-orbitals $\varphi_{2s}^g(r)$ (the pseudo 2p orbital equals here the exact 2p orbital as discussed above). The coefficients of eq. (6) are $C_{2s,1s}^g = 0.2213783$ and $C_{2s,2s}^g = 0.9509916$ for $\varphi_{2s}^g(r)$ and $C_{2p,1s}^g = 0$, $C_{2p,2p}^g = 1$ for $\varphi_{2p}^g(r)$. This choice assures that the pseudo-orbitals have near amplitude at the origin, are normalized and show maximum similarity to the exact valence orbitals (any increased mixing of $\psi_{1s}^g(r)$ into $\varphi_{2s}^g(r)$ will still assure the absence of the node in

$\varphi_{2s}^g(r)$ to deviate more significantly from $\psi_{2s}^g(r)$ in the tail region and would consequently lead to differences in the observables computed from these orbitals unless $\varphi_{2s}^g(r)$ is specifically orthogonalized to the core) [35]. It is seen from fig. 1a that for distances from the nucleus larger than about 1 bohr, $\varphi_{2s}^g(r)$ and

$\psi_{2s}^g(r)$ are very similar (relative absolute amplitude differences of less than 3%).
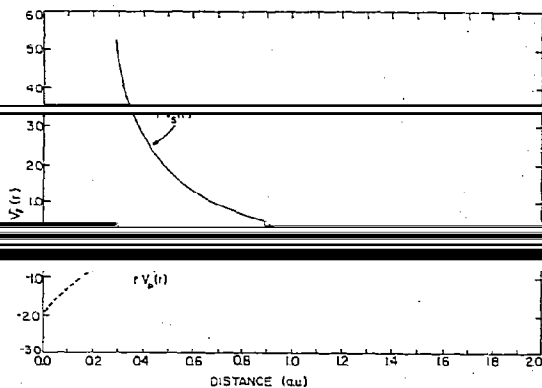
Fig. 2 depicts the pseudopotentials $V_s^g(r)$ and

Fig. 2. Pseudopotentials for carbon ——— $rV_s(r)$, – – – $rV_p(r)$.

$$V_l(r) = u_l(r) + \{V_{tot}[\rho_g(r)] - V_{tot,ps}[n_g(r)]\},$$
(25a)

where

$$V_{tot,ps}[n_g(r)] = (-Z_v/r + V_{xc,ps}^g[n_g(r)]$$
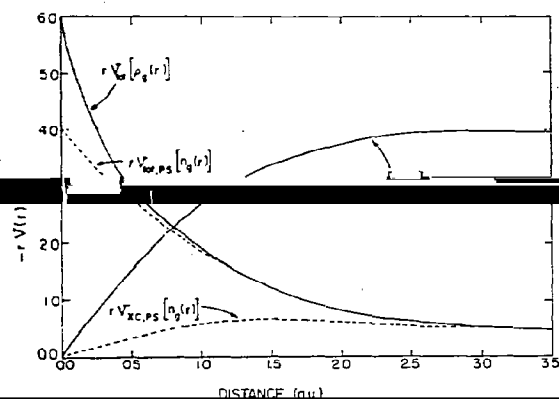
$$+ V_{Coul,ps}^g[n_g(r)]).$$
(25b)

The l-dependent non-locality appears in the first term of (25a):

$$U_l^g(r) = \epsilon_{nl}^g - \frac{\sum_{n'l} C_{nl,n'l}\psi_{n'l}^g \epsilon_{n'l}^g}{\sum_{n'l} C_{nl,n'l}\psi_{n'l}^g},$$
(26)

while the last two terms in (25a) are common to all the l-components of the pseudopotential. (This last feature arises from the locality of the LDF exchange, and does not hold in Hartree–Fock [8].) Here $V_{tot}[\rho_g(r)]$ contains the Coulomb and exchange-correlation potentials of the carbon atom and $V_{xc}^g[n_g(r)]$ and $V_{Coul}^g[n_g(r)]$ denote the

tively, associated with the pseudo-charge density. Fig.

an effective charge) together with the Coulomb and exchange-correlation components of eq. (25b).

by the small difference $V_{tot}^g[\rho_g(r)] - V_{tot,ps}[n_g(r)]$ between the Coulomb, exchange and correlation potentials corresponding to the all-electron and the pseudo-charge densities, respectively. Past a distance of about 3 au from the origin, the total Coulomb contributions to both $V_{tot}^g[\rho_g(r)]$ and $V_{tot,ps}[n_g(r)]$ are practically zero, leaving the exchange-correlation of the valence orbitals (the core contributions being already negligible at these distances) as a dominant term. As seen from fig. 3, the pseudo exchange-correlation term $V_{xc,ps}[n_g(r)]$ closely matches $V_{tot}[\rho_g(r)]$ in the tail region due to the similarity of the all-electron and pseudo-charge density [c.f. eq. (6)] in this region. The longer behavior of the pseudo-

ferences between the real and pseudo exchange-correlation potentials (which can be arbitrarily reduced through a minimization of the differences between the real and pseudo-orbitals at the tail region) [35]. The pseudopotential $V_l^g(r)$ is hence shorter range than the full all-electron potential $V_{tot}[\rho_g(r)]$ ‡.

At short distances, the non-local term $u_l^g(r)$ is core and decays rapidly to small values. For all the l-components not present in the core, the part in eq.

to mix into this nodeless valence state) and hence $u_l^g(r) = 0$, leaving a simple Lindqvist A-type potential for these states with a $-N_c/r$ dependence at small r.

In fig. 4 we display the carbon effective potential in a form more familiar in solid-state applications, i.e.

‡ We have repeated the construction of the pseudopotential including the exchange-correlation potential both from the solution of the all-electron eigenvalue problem (1) and from the pseudopotential expression (14). The results indicated that in this case the behavior of $V_l(r)$ at long range is entirely governed by the different decays of the valence Coulomb term in (25a) and the pseudo-valence Coulomb term $V_{Coul,ps}^g(r)$ of (25b). In the presence of exchange-correlation, on the other hand, the long-range behavior is dic-

with the all-electron potential $V_{tot}(r)$.

$V_{xc,ps}^g(r)$ in (25).

[36–38]. The $l \neq 0$ components ("non-local pseudo-potential") have been neglected in many solid state applications and simulated semi-empirically by the $-Are^{-\alpha r}$ form (A, $\alpha > 0$) by Hemstreet et al. [39] this is qualitatively similar to the form shown in fig. 4.

4.2. Eigenvalues and total energy differences

Tables 1 and 2 show the energy eigenvalues and the differences in total energy (excitation energies) for a series of electronic configurations for carbon [34] and tungsten [28] as obtained in an all-electron SCF calculation ("full SCF") and with the pseudopoten-

certainty in the calculation.

It is seen that a remarkably high accuracy is obtained over a large range of electronic configurations including excited and ionic species, using the ground state pseudopotential. As described above, these discrepancies are a measure of the errors introduced by frozen core approximation. To test the sensitivity of the results to the assumed reference level we recomputed the carbon pseudopotential using the $s^1 p^3$ con-

in Fourier space. The effective potential form factor

$$v_l(q) = \int \exp(-i\boldsymbol{q} \cdot \boldsymbol{r}) V_l^{\text{eff}}(r) d\boldsymbol{r} ,$$

where $V_l^{\text{eff}}(r)$ is given in eq. (9), is seen to be divergent (i.e., q^{-2}) at $q = 0$ with a cross-over ($v_s(q_0) = 0$) at $q_0 = 1.86 a_0^{-1}$ for the s-potential and a maximum ($v_s(q_m) = $ max) at $q_m = 4 a_0^{-1}$. It is more common to define these quantities relative to the Fermi wave-

eigenvalues of the tested $s^1 p^3$ eigenvalues dropped from 2×10^{-3} au to 5×10^{-8} au, while the errors in all other tested configurations did not exceed 2×10^{-3} au for the eigenvalues and 10^{-4} au for the total energy differences, confirming thereby the relative

$2k_F = 0.64$ and $q_m/2k_F = 1.37$. Numerous empirical calculations done on diamond (i.e. adjusting $v_l(G)$ to obtain agreement with experiment for some low-lying interband transition energies, where G is a reciprocal lattice vector) yield widely scattered values for the parameters of $v_l(q)$ (e.g. $q_0/2k_F = 0.725; 0.92$ and

direct first-principle values for $v_l(q)$ as predicted by the local density model for carbon (atomically screened) subject to the static 1s core approximation. In particular, we notice that our calculations show a larger pseudopotential core (i.e. smaller q_0) and more noticeably a slower decay of $v_l(q)$ with momentum at

‡ This would facilitate the use of these pseudopotentials in solid-state real-space band calculations (e.g., LCAO) since lattice sums of $V_l(r)$ converge much more rapidly than the

shows good agreement with the exact results [35].

4.3. Wavefunctions and charge densities

In table 3 we compare the calculated orbital moments using the all-electron wavefunctions ["exact orbital", $\psi_{nl}^s(r)$ of eq. (1)], the pseudo-orbitals [$\varphi_{nl}^s(r)$ of eq. (9)] and the orthogonalized pseudo-orbitals [$\tilde{\varphi}_{nl}^s(r)$ of eq. (21)] for the carbon 2s orbital. We note that the pseudo wavefunction introduces substantial errors in the moments — a factor of 4.3 in the $n = -2$

OPW) slower convergence is expected.

Hence, although the pseudo-orbital $\varphi_{nl}^{v,e}(r)$ was con-

Table 1

	E_t	−37.0536044	−5.2037811	–		E_t	−36.9274553	−5.0777439	–
	ΔE_t	0.0	0.0	–		ΔE_t	0.1261490	0.1260370	0.0001
	ϵ_{2p}	−0.1734399	−0.1755639	0.002		ϵ_{2p}	−0.3579445	−0.3593705	0.001
	E_t	−36.7533514	−4.9035473	–		E_t	−36.7741344	−4.9236569	–
	ΔE_t	0.3002530	0.3002337	0.0002		ΔE_t	0.2794699	0.2801240	0.001
$C^{1+} : s^2 p^1$	ϵ_{2s}	−0.8899874	−0.8924458	0.002	$C^0 2s^2 2p^0 3s^2$	ϵ_{2s}	−0.0943490	−0.0942194	0.00014
	ΔE_t	0.3580219	0.3573672	0.0006		ΔE_t	0.6829869	0.6828861	0.0001

structed to have the maximum possible similarity

damentally limited [c.f. eq. (6)]. This point should be

orthogonalized to the (frozen) core orbital (last column in tables 2 and 3) a remarkably high accuracy is

$10^{-4}\%$ for the ground state and less than 1% for the

perform even in polyatomic systems once the all-electron SCF problem has been replaced by the simpler

pseudopotential eigenvalue problem and should be

In table 4 we present the X-ray structure factors of carbon calculated from the ground state (frozen) core

(column 4). Again it is observed that while the use of the pseudo-orbital valence density introduces sub-

zed pseudo orbitals give rise to the correct structure

due to the normalization requirement while for very large $\sin\theta/\lambda$ all results should be identical since the

‡ The nuclear magnetic shielding constant = $\frac{1}{3}\sigma^2$

‡ This is in contrast with the results obtained by Euwema

the all-electron wavefunction and the sum extends on all electrons) is 25.8320×10^{-5} au^{-1} using the exact LDF carbon wavefunctions and, 25.4254×10^{-5} au^{-1} using the pseudo wavefunctions (1.6% error) and 25.8320×10^{-5}

1.49% error in the calculated diamagnetic susceptibility

if the orthogonalized orbitals are used.

diamond structure factors in which the use of pseudo-orbitals produced structure factors in very good agreement with these obtained from the all-electron orbitals while considerably poorer agreement was obtained when orthogonalized

principle ground-state pseudopotential is used, the ortho-

tential).

Table 2

Table 3

Energies	Pseudo-potential	All-electron	Ortho-gonalized pseudo
W^0: $6s^2 6p^0 5d^4$			
ϵ_{6s}	−0.1478	−0.1478	
ϵ_{6p}	−0.0327	−0.0327	
ϵ_{5d}	−0.1783	−0.1783	
$\langle r \rangle_{6s}$	3.4241	3.5756	3.5756
$\langle r \rangle_{6p}$	5.1157	5.2435	5.2435
$\langle r \rangle_{5d}$	1.9296	1.9996	1.9996
W^0: $6s^1 6p^1 5d^4$			
($\Delta E_t = 3.25$ eV)			
ϵ_{6s}	−0.1801	−0.1793	
ϵ_{6p}	−0.0561	−0.05579	
$\langle r \rangle_{6p}$	4.7551	4.8984	4.8781
$\langle r \rangle_{5d}$	1.8913	1.9652	1.9611
W^0: $6s^0 6p^0 5d^6$			
($\Delta E_t \approx 0.04$ eV)			
ϵ_{6s}	−0.1039	−0.1023	
ϵ_{6p}	−0.01326	−0.01278	
ϵ_{5d}	−0.07001	−0.0666	
$\langle r \rangle_{6s}$	3.8003	3.9468	3.9384
$\langle r \rangle_{6p}$	6.4531	6.7574	6.6556
$\langle r \rangle_{5d}$	2.2403	2.3089	2.3152
W^{1+}: $6s^2 6p^0 5d$			
($\Delta E_t = 9.33$ eV			
ϵ_{6s}	−0.4125	−0.4049	
ϵ_{6p}	−0.2527	−0.2471	
ϵ_{5d}	−0.5200	−0.5156	
$\langle r \rangle_{6s}$	2.9707	3.1553	3.1217
$\langle r \rangle_{6p}$	3.1722	3.9016	3.8469
$\langle r \rangle_{5d}$	1.7657	1.8434	1.8317
W^{3+}: $6s^2 6p^0 5d^1$			
($\Delta E_t = 60.22$ eV)			
ϵ_{6s}	−1.0521	−1.0386	—
ϵ_{6p}	−0.8367	−0.8121	
ϵ_{5d}	−1.3709	−1.3536	
$\langle r \rangle_{6s}$	2.4690	2.6886	2.6142
$\langle r \rangle_{6p}$	2.8443	3.0638	2.9659
$\langle r \rangle_{5d}$	1.5617	1.6471	1.6234

Moment	Pseudo-orbital	Exact orbital	Orthogonalized pseudo-orbital
C^0: $2s^2 2p^2$			
$\langle r^{-2} \rangle$	0.8214358	3.5499372	3.5494371
$\langle r^{-1} \rangle$	0.7990946	0.9135809	0.9135808
$\langle r^1 \rangle$	1.5625877	1.5938337	1.5938337
$\langle r^2 \rangle$	2.9787695	3.0896185	3.0896183
$\langle r^3 \rangle$	6.7936328	7.1030495	7.1030496
C^{1+}: $2s^2 2p^1$			
$\langle r^{-2} \rangle$	0.9051024	4.0291539	4.0570634
$\langle r^{-1} \rangle$	0.8456368	0.9771805	0.9796634
$\langle r^1 \rangle$	1.4495504	1.4815605	1.4793120
$\langle r^2 \rangle$	2.5132019	2.6221502	2.6142221
$\langle r^3 \rangle$	5.1099245	5.3930103	5.3681710
$\langle r^{-1} \rangle$	0.7825223	0.8919433	0.8919970
$\langle r^1 \rangle$	1.6227521	1.6551629	1.6558959
$\langle r^2 \rangle$	3.2845658	3.4036979	3.4066762
$\langle r^3 \rangle$	8.1686368	8.5248036	8.5353401
C^0: $2s^2 3s^2$			
$\langle r^{-2} \rangle$	0.9860846	4.5376364	4.5885756
$\langle r^{-1} \rangle$	0.8870820	1.0382943	1.0417387
$\langle r^1 \rangle$	1.3694056	1.3994561	1.3985313
$\langle r^2 \rangle$	2.2264337	2.3252487	2.3733574
$\langle r^3 \rangle$	4.7719507	4.4611905	4.4581860
C^0: $2s^1 2p^3$			
$\langle r^{-2} \rangle$	0.8293108	3.5802110	3.5972737
$\langle r^{-1} \rangle$	0.8035044	0.9177704	0.9197704
$\langle r^1 \rangle$	1.5514342	1.5855766	1.5825911
$\langle r^2 \rangle$	2.9313405	3.0535451	3.0413864
$\langle r^3 \rangle$	6.6152805	6.9637727	6.9199654

that the errors introduced by using the nonortho-gonalized pseudo-orbitals are quite sizable and substantially larger than the accuracy of most experimental structure factor measurement techniques.

Although one has broad latitude in choosing the coefficients $C_{nl,n'l}$, particular choices may have special advantages or disadvantages [5−8,35,41−44]. The choice actually made above (adding just enough core to remove the first node) or suggested later (adding enough core to make the pseudo valence large-r region) are obvious ones, as long as the final valence orbitals are reorthogonalized to the core, no

e.g. −1.8% at $\sin \theta/\lambda = 2.1$ a_0^{-1} and positive at medium $\sin \theta/\lambda$, e.g. 5.4% at $\sin \theta/\lambda = 13.6$ a_0^{-1}.) We note

Table 4

X-ray structure factors for the ground state carbon atom

$S_{lu \, v}/\pi$ (a_0^{-1})	f^{exact}	f^{pseudo}	$f^{pseudo-orth}$
0.0	6.000000	6.000000	6.000000
0.3	5.778677	5.781887	5.778679
0.6	5.210876	5.222423	5.210886
1.0	4.254419	4.279708	4.254418
1.5	3.199111	3.236315	3.199107
2.1	2.374506	2.411824	2.374506
2.8	1.879442	1.902297	1.879443
3.6	1.614311	1.614498	1.614311
4.5	1.442790	1.421250	1.442791
5.5	1.282316	1.246075	1.282316
7.8	0.925535	0.883754	0.925535
10.5	0.591291	0.560647	0.591291
13.6	0.348089	0.329355	0.348089
19.0	0.146508	0.138699	0.146508
30.0	0.035460	0.633669	0.035461

Table 5

Carbon ground state eigenvalues and moments of r in the 2s state, computed with the pseudopotential of eq. (27). The results are compared with the exact all-electron solutions, eq. (1). Energies in atomic units and $\langle r^n \rangle$ in a_0^n

	Effective potential	Full SCF
ϵ_{2s}	−0.4573829	−0.4573838
ϵ_{2p}	−0.157951	−0.1579534
$\langle r^{-2} \rangle$	64.1055643	3.5499372
$\langle r^{-1} \rangle$	5.5995528	0.9135809
$\langle r \rangle$	0.2730326	1.5938337
$\langle r^2 \rangle$	0.10104083	3.0896185

particularly serious errors in the calculated charge distribution occur (table 3). This will be true, generally, so long as the $C_{nl,n'l}$ are chosen with reasonable caution. One extreme choice of the $C_{nl,n'l}$ permits comparison with the Phillips—Kleinman pseudopotential.

$$V_f^s(r) = (\epsilon_{2s} - \epsilon_{1s})|l = 0\rangle\langle l = 0|$$
$$+ V_{tot}^g[\rho_g(r)] - V_{tot,ps}^g[n_g(r)] . \qquad (27)$$

Notice that this result has the form of the Phillips—Kleinman potential [4]: the first (pseudopotential) term accounts for the orthogonality and drives the orbital energy up to the correct value, while the last

hand, the ψ_{1s} is not very much like φ_{2s} in the tail region, so that the resulting pseudopotential (27) would be expected to yield rather poor wavefunctions and orbital densities; again, table 5 shows this expectation to be coreect. In this case, however (unlike the choices taken previously for the $C_{nl,n'l}$), we cannot simply reorthogonalize the valence to the core, since we choose $\varphi_{2s} = \psi_{1s}$, so that the valence orbital *is* the core orbital. Thus, although the choice

of $C_{nl,n'l}$ is arbitrary and unimportant in some limits, extreme choices like this one can lead to poor results for *wavefunction* quantities, even though the *orbital energies* are very satisfactory. This must be kept in mind when using empirically-derived pseudopotentials for calculating such observables as charge densities, oscillator strengths or Compton profiles.

Table 2 presents additional results, for the tungsten atom [28]. Again, the first-principles pseudopotential reproduced energy quantities to extremely high accuracy, while the pseudo wavefunction reorthogonalized to the frozen core yields excellent moments; even for this stringent test, on a large system with occupied high angular momentum states and at high excitation energies, our pseudopotential performs admirably.

state, the errors are no larger than 2%. Thus even for this stringent test, on a large system with occupied high angular momentum states and at high excitation energies, our pseudopotential performs admirably.

5. Remarks

procedures for use in the LDF context [34,35,45—48]. Several of these pseudopotential methods are semi-empirical [36—38] and are subject to some errors, particularly for wavefunction-related quantities [49,50]; we feel that these failures are due to both the failure to include the full angular momentum dependence and the absence of explicit constraints of wavefunction similarity. More recently, several first-principles pseudopotential-LDF procedures have been proposed

[34,35,45,46], some of which have been successfully tested in molecular [50] or solid-state [51] calcula-

retains the symmetry of the spherical harmonic expansion about each center, enjoys some efficiency advantages, particularly for band-structure studies employing plane-wave or gaussian basis sets [51] over procedures [45] which actually employ the differences between pseudo-densities and true valence densi-

and the method employing density differences may actually be preferable. Both our method and those developed by Snijders and Baerends [45] and by

fitting of experimental data, and do not make (often unjustifiable) oversimplifications in the treatment of the higher l-components of the pseudopotential; as expected on the basis of our formal arguments, first-principles potentials of the present type seem noticeably superior to earlier semi-empirical potentials for

tion [34,35]. The pseudopotentials are straightforward to calculate once an exact solution to the all-elec-

state of the atom is available, and should offer great

polyatomic systems. Tests for the performance of the atomic pseudopotential for the C and W atoms in predicting excited-state properties show accuracy better than 2×10^{-3} au for eigenvalues and 10^{-3} au for total energy differences for an excitation energy range up to 10 eV. While the direct use of the self-consistent pseudo-orbitals to compute orbital mo-

negligible errors, a simple orthogonalization procedure was shown to produce excellent agreement with

first-row atoms are equally satisfactory, and are pres-

and some calculations on diatomic molecules [52] indicate that the present method does indeed produce a useful, viable, efficient, accurate first-principles LDF pseudopotential.

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