### ON THE FIRST PRINCIPLES HARTREE-FOCK AND LOCAL DENSITY PSEUDOPOTENTIALS\*

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Angular momentum projected Hartree-Fock (HF) and local density functional (LDF) nonlocal atomic pseudopotentials are derived from first principles in a way that allows their comparison. It is found that in both cases the pseudopotential is given by a term which vanishes for angular momenta species not present in the core and is strongly repulsive otherwise, plus a term that represents the difference between an averaged total (all-electron) and valence potentials. It is shown that: (a) the HF and LDF pseudopotentials behave very similarly in the entire space, contrary to the marked differences in the corresponding all-electron potentials. This is due to both the cancellation of the self-interaction term in the LDF pseudopotential form and the localization of the (otherwise state dependent) HF exchange; (b) while the HF pseudopotentials for the different l-components not present in the core are in general different, the analogous LDF pseudopotentials are identical; (c) the energy dependence of both pseudopotentials is small; (d) by properly determining the pseudowavefunctions from the allelectron exact orbitals, it is possible to reduce the long tails of these pseudopotentials in momentum space, making them useful for methods that solve the associated single-particle equations in reciprocal space, with only small errors introduced into the valence part of the pseudowavefunctions; (e) the "transition state" theorem, which holds for the all-electron LDF, applies similarly to LDF pseudopotential results. We discuss the detailed comparison between the HF and LDF pseudopotential and their relation to the Phillips-Kleinman form. It is seen that for the HF scheme, these can be made identical only for the bare core. Generally, the Phillips-Kleinman method will produce substantial structure in the potential and/or in the pseudowavefunction; this additional structure causes computational difficulties, such as the need to include extra basis functions. More serious is the fact that the original Phillips-Kleinman procedure applies only for single-valence-electron ions, which may be poor models for the right half of the periodic table.

### 1. Introduction

Nearly all qualitative discussion of chemical bonding, of structural and transport properties of condensed phases, of optical, magnetic resonance and vibrational spectroscopy, and of molecular response properties and reactivities are presented with reference to the valence electrons of the system. For such discussions, one usually omits entirely specific consideration of the core electrons, since their tight binding character (always at least several volts greater than valence electrons) and their approximately spherical symmetry make them nearly unresponsive to any low energy (bonding) perturbations. Indeed, the notion of chemical periodicity is based on this essential passivity of core electrons to changes in bonding environment. When, however, one attempts quantitative description of the electronic structure of atoms, molecules or solids, the core electrons can no longer simply be omitted from explicit consideration. For example, one clearly cannot approximate the Schrödinger equation for Li by that for H.

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The straightforward solution to this problem is simply to include the core electrons in any electronic structure calculation, so that, for instance,  $Na_2$  becomes a 22-electron problem.

This approach is feasible and successful, and forms the basis for nearly all rigorous ab initio or first principles electronic structure calculation \*. Nevertheless, one feels, on the basis of the stability of the core levels and the generality of periodic behavior, that this explicit reckoning of the core levels is redundant.

Many techniques for circumventing the inclusion of core levels have been proposed. The most straightforward involves neglecting the core electrons, but modifying the valence hamiltonian, or, equivalently, its matrix elements within any chosen basis set. This is the scheme employed in most semi-empirical electron structure methods [PPP (cf. ref. [3]), CNDO (cf. ref. [4]), extended Hückel (cf. ref. [5])] and underlies many of the model hamiltonians (Hubbard [6], tightbinding, Heisenberg) commonly employed in discussion of solid-state electronic structure. Most of these schemes are semi-empirical, with the relevant matrix elements parametrized to describe any given desired set of experimental data. A closely related approach, often referred to as the empirical pseudopotential procedure, has been of great utility [7] in describing the band structure of a large number of solids. In this scheme, one fixes certain Fourier components of the potential due to the core electrons acting in the valence space, by matching experimental data such as interband transition energies. Once this empirical pseudopotential information is acquired, however, the valence behavior is treated in a first-principles fashion. Thus the empirical pseudopotential scheme forms a bridge between the semi-empirical model hamiltonian approach and the use of nonempirical, first-principles pseudopotential methods.

Pseudopotential schemes are based on the notion that the effects of the core orbitals on the valence electrons can be approximated by an effective one-electron operator, replacing both the full Coulombic and the Pauli interaction of valence with core. Pseudopotentials were introduced by Hellmann [8] and by Gombas [9],

but these spherically symmetric potentials were quantitatively satisfactory only for cases of one or possibly two valence electrons. The reason for this was elucidated by Phillips and Kleinman [10], who pointed out that since there are both Coulomb and Pauli interactions between core and valence orbitals, the proper pseudopotentials must also account for both of these effects. For example, in a first row atom, the 2s function is constrained by the Pauli principle to be orthogonal to the 1s core function, whereas the 2p wavefunction is automatically orthogonal by virtue of its differing angular momentum. Thus the effective core potential felt by  $\Psi_{2s}$  would be expected to be repulsive in the core region due to the Pauli (orthogonality) condition, while that felt by  $\Psi_{2p}$  should be attractive near the nucleus, where the 1s orbital no longer efficiently screens the core charge. Phillips and Kleinman [10] thus proposed a nonlocal pseudopotential operator involving a core orbital projector, of the form  $\Sigma_{\rm c}(\epsilon_{\rm v}-\epsilon_{\rm c})|\Psi_{\rm c}\rangle\langle\Psi_{\rm c}|$ , where  $\epsilon_{\rm v}$  and  $\epsilon_{\rm c}$  are the core and valence energies and  $\Psi_c$  is a core orbital. These pseudopotentials were originally proposed to account only for the Pauli barrier (to remove the constraint of core orthogonality by means of an operator added to the hamiltonian for a single valence electron), although formal generalizations to several valence electrons (e.g. ref. [11]) as well as parametrized forms which included an approximation to the core-valence Coulomb interaction [12] were soon forthcoming. The use of these core-projection type pseudopotentials has become very widespread in Hartree-Fock-Roothaan molecular orbital calculations in recent years [12,13]; the methods of Huzinaga [12], in particular, have been quite successful for a number of molecules.

Since the Pauli principle constraint in atoms can be expressed in terms of angular momentum symmetry, a number of pseudopotential methods have been introduced [14-20] which utilize an angular momentum projection pseudopotential on each atom, of the form  $\Sigma_{lm} V_{lm}(r) |lm\rangle \langle lm|$ . Here  $V_{lm}(r)$  is a smooth function of the radial distance, and l, m are the orbital angular momentum and its component. This potential is intended to represent both Coulomb and Pauli effects of the core on the valence electrons. Such potentials have been developed independently by a number of workers, especially by Kahn, Goddard and Melius [14, 15], for utilization within Hartree-Fock-Roothaan calculations. Several successful studies em-

<sup>\*</sup> An excellent survey of HF molecular studies is given by Schaefer [1]. No such comprehensive review of LDF calculations is available, but extensive references are given in ref. [2].

ploying these potentials both at the single-determinant [16-19,21-25] and correlated wavefunction [18,26] level have been reported, and these potentials now appear to allow accurate, first-principles valence-only Hartree-Fock-Roothaan calculations for many molecular systems. In particular, the paper by Kahn et al. [16] contains an especially clear discussion of the angular-momentum-projector pseudopotentials, and a lengthy reference list.

Very recently, specifically designed pseudopotentials, both of Phillips-Kleinman (core projection) type [27] and of angular momentum projector types [28], have been introduced for use in conjunction with Hohenberg-Kohn-Sham [29] local density functional (LDF) calculations. The LDF method involves solution of a one-electron eigenvalue equation of Hartree-Fock type, except that the nonlocal exchange potential of the Fock operator is replaced by a local exchange-correlation potential, which is a functional of only the total electron density. The LDF method is widely used in first-principles [30-33] and empirical [7.34] band theoretic studies, and its application to atomic and molecular problems is becoming widespread [35-37]. The applicability of pseudopotentials within this scheme must, however, be justified in a slightly different way than is done for Hartree-Fock; indeed, Slater [38] even questioned this applicability on a priori grounds, although the multiple scattering procedure he developed must be distinguished from . LDF per se.

The present paper presents a comparison of the role and nature of pseudopotentials within the Hartree— Fock (HF) and the LDF methods. It attempts to clarify the nature and utility of, and differences between, the LDF and HF first-principles pseudopotentials. We show that the use of pseudopotentials within LDF can be rigorously justified, and indeed, that in some senses the pseudopotential method, which is based on replacing the local effects of the core by a smooth potential [39], is more in keeping with the local potential picture of LDF than with the nonlocal exchange potential of HF [28]. We also demonstrate the great similarity of LDF and HF angular-momentum dependent pseudopotentials, both of which contain an average, *l*-independent potential and a weak *l*-dependent part.

We feel that first-principles pseudopotential methods are of great practical value in permitting rigorous valence-only calculations to be completed using both

LDF and HF methods; the present paper constitutes a comparison, derivation and partial evaluation of these methods; numerical results using pseudopotential HF [14–26] and pseudopotential LDF [28] are reported elsewhere. Sections 2 and 3 present unified derivations of the HF and LDF angular-momentum projected pseudopotentials, respectively; section 4 compares the potentials so obtained. Section 5 examines the general applicability of the pseudopotentials in real systems, by consideration of the angular momentum dependence, of the relation to the frozen core approximation, of the energy dependence of the pseudopotential and of the superposition-of-atomicpseudopotentials step which must be made for applications to molecules or solids. Section 6 contrasts these angular-momentum projected pseudopotentials to the Phillips-Kleinman core-projection type which, we feel, have some serious drawbacks. Finally, section 7 contains brief concluding remarks.

# 2. Development of HF pseudopotentials

Let the HF hamiltonian for the atomic (central field) valence state *nl*, in some chosen reference electronic state g, be denoted (using Hartree atomic units) as

$$H_{nl}^{g} = -\frac{1}{2}\nabla^{2} + V_{nl}^{g, \text{tot}}, \qquad (1)$$

where the total HF potential, partitioned into "core" and "valence" parts, is:

$$V_{nl}^{g_{t}tot} = V_{nl}^{g_{t}c} + V_{nl}^{g_{v}v}$$

$$= \left[ -Z_{c}/r + \sum_{n'l'}^{core} 2J_{n'l'}^{c} - K_{n'l'}^{c} \right]$$

$$+ \left[ -Z_{v}/r + G_{nl}(\{\psi_{n'l'}^{g_{v}v}\}) \right].$$
(2)

Here  $Z_c$  denotes the number of core electrons and  $Z_v = Z - Z_c$ .  $J_{n'l}^{g_c}$  and  $K_{n'l'}^{g_c}$  denote the Coulomb and exchange integrals of core state n'l' in the reference configuration g (the primed sum indicating exclusion of self-interaction terms) and  $G_{nl}(\{\psi_{n'l'}^{g_c}\})$  denotes collectively the valence-valence interactions, which depend on the entire valence manifold  $\{\psi_{nl'}^{g_cv}\}$ , i.e., for an (ns, n'd) transition metal atom,

$$G = J_{ns}^{g,v} + \sum_{m_l} (J_{nd,m_l}^{g,v} - \frac{1}{2} K_{nd,m_l}^{g,v}),$$

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and for a single valence electron atom G = 0. The Coulomb integral  $J_{nl}^g$  is given by the classic electrostatic potential

$$J_{nl}^{g}(r) = \int \frac{\psi_{nl}^{*g}(r') \psi_{nl}^{g}(r')}{|r-r'|} \,\mathrm{d}r' \,, \tag{3}$$

while the exchange potential  $K_{nl}^g(r)$  is a level-dependent nonlocal operator:

$$K_{n'l'}^{\mathbf{g}}(\mathbf{r}) \psi_{nl}^{\mathbf{g}}(\mathbf{r}) = \psi_{q'l'}^{\mathbf{g}} \int \frac{\psi_{nl}^{\mathbf{g}}(\mathbf{r}') \psi_{nl'}^{\mathbf{g}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r}' \,. \tag{4}$$

The eigenvalue equation for a valence state  $\psi_{nl}^{g,v}$  is given by

$$H_{nl}^{g}\psi_{nl}^{gv} = \epsilon_{nl}^{gv}\psi_{nl}^{gv} .$$
<sup>(5)</sup>

The usual requirement of the orthogonality of the valence orbitals  $\{\psi_{nl}^{g_V}\}$  to the core orbitals  $\{\psi_{nl}^{g_V}\}$  results in the familiar nodal behavior of  $\psi_{nl}^{g_V}$  and in the need to use a rather large basis set (e.g., analytic atomic-like orbitals or plane waves) for their representation. One hence proceeds [10,11,14] by requiring that the valence set  $\{\psi_{nl}^{g_V}\}$  be replaced by a pseudo-orbital set  $\{\varphi_{nl}^{g}\}$  made up of combinations of the all-electron eigenfunctions: The radial part of this "pseudo-orbital",  $\Phi_{nl}^{g}$  is given in terms of the HF radial orbitals  $R_{nl}$  as

$$\Phi_{nl}^{g} = C_{nl,nl}^{g} R_{nl}^{g,v} + \sum_{n'}^{\text{core}} C_{nl,n'l}^{g} R_{n'l}^{g,c}$$
$$= \sum_{n'}^{\text{core}+1} C_{nl,n'l}^{g} R_{n'l}^{g,c}, \qquad (6)$$

where the coefficients  $\{C_{nl,n'l}^g\}$  are chosen so that  $\varphi_{nl}^g$  has some desired features, e.g., be nodeless and close to the original  $\psi_{nl}^{gv}$  [28], or have minimum kinetic energy [14-16], etc. Note that only  $R_{n'l}$  orbitals belonging to the same *l* as in  $\Phi_{nl}^g$  are required in the sum. One then replaces the HF hamiltonian for the valence orbitals in (1) by a pseudo-hamiltonian

$$H_{nl}^{g,PS} = -\frac{1}{2}\nabla^2 + V_{nl}^{g,eff}(\mathbf{r}), \qquad (7)$$

where the effective potential  $V_{nl}^{g,eff}(\mathbf{r})$  for orbital nl in state g can be partitioned into a valence field plus an external potential

$$V_{nl}^{g,eff} = V_{nl}^{g,v} + V_{nl}^{g,PS} , \qquad (8)$$

and the valence potential  $V_{nl}^{gv}$  has the form (2). Since by changing the HF potential for the valence orbitals from  $V_{nl}^{g}$  in (2) to  $V_{nl}^{geff}$  in (8) and requiring that for the reference state g one obtains (6) as eigenfunctions one can still obtain any eigenvalue spectra, one uses this freedom, requiring that  $H_{nl}^{gPS}$  in (7) would have the same spectrum as  $H_{nl}^{g}$ , for state g [eq. (5)] i.e.,

$$H_{nl}^{\mathbf{g},\mathbf{PS}}\varphi_{nl}^{\mathbf{g}} = \epsilon_{nl}^{\mathbf{g},\mathbf{v}}\varphi_{nl}^{\mathbf{g}} \,. \tag{9}$$

This defines the pseudopotential in (8) in terms of the valence energy  $\epsilon_{nl}^{gv}$ , the pseudo-orbital  $\varphi_{nl}^{g}$  and the valence potential, as

$$V_{nl}^{g,\text{PS}} = \epsilon_{nl}^{g,v} + \frac{1}{2} \frac{\nabla^2 \varphi_{nl}^g}{\varphi_{nl}^g} - \frac{V_{nl}^{g,v} \varphi_{nl}^g}{\varphi_{nl}^g} .$$
(10a)

For a central-field problem, the pseudopotential can be represented in terms of the radial pseudo-orbitals  $\Phi_{nl}^g$  and the associated kinetic operator as

$$V_{nl}^{g,PS} = \epsilon_{nl}^{g,v} + \frac{1}{2} \frac{\nabla_r^2 \Phi_{nl}^g}{\Phi_{nl}^g} - \frac{V_{nl}^{g,v} \Phi_{nl}^g}{\Phi_{nl}^g} - \frac{1}{2} \frac{l(l+1)}{r^2}.$$
 (10b)

The forms (9) and (10) have been used in numerous calculations on atoms and molecules to replace the original equation (1). For a system with one-electron outside a filled core, (10) yields

$$V_{nl}^{g,PS} = \epsilon_{nl}^{g,v} + \frac{1}{2} \frac{\nabla_r^2 \Phi_{nl}^g}{\Phi_{nl}^g} - \frac{1}{\Phi_{nl}^g} \left( -\frac{Z_v}{r} + J_{nl}^{g,v} - \frac{1}{2} K_{nl}^{g,v} \right) \Phi_{nl}^g, \qquad (11)$$

while for a bare closed shell ionic core, this simply reduces to

$$V_{nl}^{g,PS} = \epsilon_{nl}^{g,v} + \frac{1}{2} \frac{\nabla_r^2 \Phi_{nl}^g}{\Phi_{nl}^g} - \left(-\frac{Z_v}{r}\right).$$
(12)

When the effective potential (8) is generated from (11) and (12) for the *reference state* g, the terms in the curly brackets tend to cancel against  $V_{nl}^{gv}$ , while when applied to *a general state*  $s \neq g$ , these terms persist.

We now rewrite the second terms in (10b) in a different form. Using the fact that the orbitals  $\psi_{nl}^g$  entering the pseudo-orbital definition (6) are eigenfunctions of the original HF hamiltonian [eqs. (1) and (5)], we write

$$\frac{1}{2}\nabla^2 \psi_{n'l'}^{g} = (V_{n'l'}^{g,\text{tot}} - \epsilon_{n'l'}^{g}) \psi_{n'l'}^{g}, \qquad (13a)$$

or, for the radial component  $R_{n'l'}^{g}$ :

$$\frac{1}{2}\nabla_r^2 R_{n'l'}^{g} = \left( V_{n'l'}^{g,\text{tot}} + \frac{1}{2} \frac{l'(l'+1)}{r^2} - \epsilon_{n'l'}^{g} \right) R_{n'l'}^{g} .$$
(13b)

Define now the "average" total potential function as

$$\langle V_{nl}^{g,tot}(\mathbf{r}) \rangle = \left[ \sum_{n'}^{c+1} C_{nl,n'l}^{g} V_{n'l}^{g,tot}(\mathbf{r}) R_{n'l}^{g}(\mathbf{r}) \right] \\ \times \left[ \sum_{n'}^{c+1} C_{nl,n'l}^{g} R_{n'l}^{g}(\mathbf{r}) \right]^{-1},$$
 (14a)

the average energy eigenvalue function as

$$\langle E_{nl}^{g}(r) \rangle = - \left[ \sum_{n'}^{c+1} C_{nl,n'l}^{g} \epsilon_{n'l}^{g} R_{n'l}^{g}(r) \right] \\ \times \left[ \sum_{n'}^{c+1} C_{nl,n'l}^{g} R_{n'l}^{g}(r) \right]^{-1} ,$$
 (14b)

and the average centrifugal potential as

$$\langle P_{nl}^{g}(r) \rangle = \left[ \sum_{n'}^{c+1} C_{nl,n'l}^{g} \frac{1}{2} \frac{l(l+1)}{r^{2}} R_{n'l}^{g}(r) \right] \\ \times \left[ \sum_{n'}^{c+1} C_{nl,n'l}^{g} R_{n'l}^{g}(r) \right]^{-1} ,$$
 (14c)

where the index c + 1 indicates summation on the core (c) plus a single valence orbital *nl*. One obtains for the second term in (10b)

$$\frac{1}{2} \frac{\nabla_r^2 \Phi_{nl}^g}{\Phi_{nl}^g} = \langle V_{nl}^{g,\text{tot}}(\mathbf{r}) \rangle + \langle P_{nl}^g(\mathbf{r}) \rangle + \langle E_{nl}^g(\mathbf{r}) \rangle, \quad (14\text{d})$$

and the pseudopotential becomes

$$V_{nl}^{g,PS}(r) = [\epsilon_{nl}^{g,v} + \langle E_{nl}^{g}(r) \rangle] + \langle V_{nl}^{g,tot}(r) \rangle - \langle V_{nl}^{g,v}(r) \rangle, \qquad (15)$$

where the term  $\langle P_{nl}^{g}(r) \rangle - \frac{1}{2}l(l+1)/r^2$  drops since  $l(l+1)/r^2$  multiples all  $R_{n'l}^{g}$  in (14c) as a constant, and  $\langle V_{nl}^{gv}(r) \rangle$  is defined as in (14a) but for the valence field  $V_{nl}^{gv}$  only.

The first term in brackets in (15) can be written as

$$U_{nl}^{g}(r) = \epsilon_{nl}^{g,v} + \langle E_{nl}^{g}(r) \rangle$$
$$= \left[ \sum_{n'}^{c} \left( \epsilon_{nl}^{g,v} - \epsilon_{nl}^{g,c} \right) C_{nl,n'l}^{g} R_{n'l}^{g'}(r) \right]$$

$$\times \left[\sum_{n'}^{c+1} C_{nl,n'l}^{g} R_{n'l}^{g}(r)\right]^{-1}, \qquad (16)$$

which takes the form of the Phillips--Kleinman repulsive potential [10] for a particular choice (6) of the coefficients  $C_{nl,n'l}^{g}$ . The final expression is hence

$$V_{nl}^{g,PS}(\mathbf{r}) = U_{nl}^{g}(\mathbf{r}) + \langle V_{nl}^{g,tot}(\mathbf{r}) \rangle - \langle V_{nl}^{g,v}(\mathbf{r}) \rangle .$$
(17)

The average total and valence potential [last two terms in (17)] depend on the particular pseudo-orbital indices *nl*, since the HF potential in (14a) is state dependent [c.f. eq. (4)]. The pseudopotential can be computed directly from (17) using the forms (14a) and (16), or alternatively from (12) by direct application of the kinetic operator to the corresponding orbitals. Expression (17) has however the theoretical advantage in that it demonstrates the type of averages involved in going from the nonlocal form of  $V_{nl}^{g,tot}$  in (5) to the local form (17) and in revealing the nature of  $V_{nl}^{g,PS}(r)$  as a *core-like* potential (i.e., containing differences between total and valence potentials).

We have transformed the original all-electron eigenvalue problem (5) to another problem (9) having a valence field  $V_{nl}^{g,v}$  like the original problem, plus an additional potential  $V_{nl}^{g,PS}$  (17), where the new problem has the same valence spectrum  $\epsilon_{nl}^{gv}$  as the original problem, but with "smooth" eigenfunctions given by (6). The construction of  $V_{nl}^{g,P5}$  requires knowledge of the all-electron eigenvalues and eigenfunctions for state g and hence the use of (9) has no practical advantage over the use of (5), for this state. The usefulness of these pseudopotentials lies entirely in the question whether one can use  $V_{nl}^{g,PS}$  to replace the core electrons for atomic states other than those used to generate  $V_{nl}^{g,PS}$ , as well as for atoms in bonding states in molecules and solids. We will postpone the discussion of this question until after the discussion of the pseudopotential generated from the local density theory.

### 3. Development of LDF pseudopotentials

The local density formalism of Hohenberg and Kohn [29] and Kohn and Sham [40] rests on the fundamental theorem that in the presence of an external potential field  $W_{ext}(r)$ , the total energy of an interacting inhomogeneous electron system (including correlation) can be written as

$$E = \int W_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) \, \mathrm{d}\mathbf{r} + F[\rho(\mathbf{r})] , \qquad (18)$$

where  $F[\rho(r)]$  is a universal functional of the density  $\rho(r)$ , *independent* of the external potential, and that for the correct ground state density, E is a minimum. This theorem forms the basis for an entire electronic structure theory in that it provides an effective one-particle equation (derived by applying variation to (18) with respect to  $\rho(r)$ , and replacing the function derivative of the non-interacting kinetic energy, by the exact quantum mechanical laplacian) of the form

$$\left\{-\frac{1}{2}\nabla^2 + W_{\text{tot}}[\rho(\mathbf{r})]\right\}\psi_{nl}^{g} = \epsilon_{nl}^{g}\psi_{nl}^{g} \tag{19}$$

(we consistently denote LDF potentials by W and HF potentials by V; note that the LDF  $\psi$  of (19) and the HF  $\psi$  of (5) will differ). The total potential in the ground electronic state g is given by

$$W_{\text{tot}}[\rho_{g}(\boldsymbol{r})] = W_{\text{ext}}(\boldsymbol{r}) + W_{\text{coul}}[\rho_{g}(\boldsymbol{r})] + W_{\text{xc}}[\rho_{g}(\boldsymbol{r})], (20)$$

where, for an all-electron calculation  $W_{\text{ext}}(r)$  is usually identified with the electron-nuclear term -Z/r and the Coulomb potential is just a sum of the  $J_{nl}^{g}$  terms (3) over the occupied states:

$$W_{\rm coul}[\rho_{\rm g}(r)] = \int \frac{\rho_{\rm g}(r')}{|r-r'|} \, \mathrm{d}r' = \sum_{nl}^{\rm occ} N_{nl} J_{nl}^{\rm g} \,, \qquad (21)$$

where  $N_{nl}$  are the occupation numbers. The last term in (20) represents the total exchange and correlation potential. In lowest order in the gradient expansion [40], it is given by

$$W_{\rm xc}[\rho_{\rm g}(r)] = W_{\rm x}[\rho_{\rm g}(r)] + W_{\rm c}[\rho_{\rm g}(r)]$$
, (22)

where  $W_{\rm x}[\rho_{\rm g}(\mathbf{r})]$  is the well known " $\rho^{1/3}$ " term

$$W_{\rm x}[\rho_{\rm g}(r)] = -(3/\pi)^{1/3} [\rho_{\rm g}(r)]^{1/3}$$
, (23)

while the free-electron correlation potential  $W_c[\rho_g(r)]$ is a more complicated functional of  $\rho(r)$ , given by many authors [41-43]. The total energy is given in the LDF formalism as

$$E = \sum_{i}^{\text{occ}} N_{i} \epsilon_{i} - \frac{1}{2} \iint \frac{\rho_{g}(\mathbf{r}) \rho_{g}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathrm{d}\mathbf{r} \, \mathrm{d}\mathbf{r}'$$
$$- \int \rho_{g}(\mathbf{r}) \, W_{\text{xc}}[\rho_{g}(\mathbf{r})] \, \mathrm{d}\mathbf{r} + E_{\text{xc}}[\rho_{g}(\mathbf{r})] \,, \qquad (24)$$

where the total exchange and correlation energy  $E_{\rm xc}[\rho(\mathbf{r})]$  is related to the corresponding potential  $W_{\rm xc}[\rho_{\rm g}(\mathbf{r})]$  by

$$W_{\rm xc}[\rho_{\rm g}(\mathbf{r})] = \delta E_{\rm xc}[\rho_{\rm g}(\mathbf{r})]/\delta \rho_{\rm g}(\mathbf{r}) . \tag{25}$$

In principle, the LDF theorem assures that given the form of  $E_{xc}[\rho(\mathbf{r})]$ , one can generate the potential (20), solve (19) self-consistently and obtain the exact variational total energy (24) of the system, and the ground state observables related to  $\rho(\mathbf{r})$ . In practice, despite extensive work on the related many-body theory [41–43], the form of  $E_{xc}[\rho(r)]$  for a general form of  $\rho(\mathbf{r})$  is not known yet, and one has to resort to approximate forms [such as those leading to (22)-(23)] that are exact only for some limiting forms of  $\rho(\mathbf{r})$  (e.g., slowly varying density [40]). Despite this limitation, one finds that when some of the rather drastic computational approximations (i.e., muffintin approximations to  $W_{tot}[\rho(r)]$  [44], non-self-consistency or basis set limitations), previously involved in solving (19) with the functionals (22)–(23) are eliminated, extremely useful results are obtained for ground state properties of molecules [35-37] and solids [30-33,46], such as binding energies, lattice constants, bulk moduli, Compton profiles, X-ray scattering factors and magnetic moments. In particular, detailed comparison of careful restricted HF and LDF calculations on solids such as diamond [31], LiF [32] and boron nitride [33] and diatomic molecules [35], has revealed a clear superiority of the latter for most properties. However, when the simplifying assumptions of spherical site symmetry of  $W_{tot}[\rho(\mathbf{r})]$  used in "standard" augmented plane wave [46], multiple scattering Xa [44] or linear muffin-tin orbitals [47] is relaxed, the all-electron solution of (19) becomes rather involved, mainly due to the need to compute the many center integrals of  $W_{coul}[\rho(\mathbf{r})]$  over some basis set, and the corresponding integrals for  $W_{\rm xc}[\rho(\mathbf{r})]$  that are not simply reducible to a manycenter form. Hence, a pseudopotential reduction of (19) to a valence electron problem becomes advantageous.

To do that, we consider a fictitious (pseudo) atom in the reference (valence) electronic state g, having  $N_v$ electrons (where  $N_v$  is the number of valence electrons in the real atom) which move in an external field  $W_{\text{ext}}(r) = -Z_v/r + W_{Rl}^{g,\text{PS}}(r)$  and the Coulomb and exchange correlation field,  $W_{\text{coull}}[n_g(r)]$  and  $W_{\text{xc}}[n_g(r)]$ , respectively. We denote by n(r) the charge density of the pseudosystem, and by  $\rho(r)$  the all-electron charge density. We shall require that the eigenfunctions of this system, in state g, take the form (6) and that the valence eigenvalue spectra for g be identical to that produced by the corresponding all-electron hamiltonian described by (19). Hence we set a modified eigenvalue problem

$$\{-\frac{1}{2}\nabla^2 - Z_v/r + W_{nl}^{g,PS}(r) + W_{coul}[n_g(r)]$$
  
+  $W_{xc}[n_g(r)]\} \varphi_{nl}^g = \epsilon_{nl}^g \varphi_{nl}^g,$  (26)

where the self-consistent density is given by

$$n_{\rm g}(r) = \sum_{nl}^{\rm occ} N_{nl}^{\rm v} |\varphi_{nl}^{\rm g}(r)|^2 , \qquad (27)$$

and  $N_{nl}^{v}$  are the occupation numbers for the pseudoatom (identical to that of the valence orbitals in the real atom). Solving for the unknown potential in (26), we get

$$W_{nl}^{g,PS}(r) = \epsilon_{nl}^{g,v} + \frac{1}{2} \frac{\nabla^2 \varphi_{nl}^g}{\varphi_{nl}^g} - \{-Z_v/r + W_{coul}[n_g(r)] + W_{xc}[n_g(r)]\}, \quad (28)$$

and, using the fact that the all-electron orbitals  $\psi_{nl}^{g}$  entering the definition of the pseudo-orbital  $\varphi_{nl}^{g}$  in (6) are eigenfunctions of the total LDF hamiltonian (19), we get for the radial part  $\Phi_{nl}^{g}$ :

$$\frac{1}{2} \frac{\nabla_r^2 \Phi_{nl}^g}{\Phi_{nl}^g} = W_{\text{tot}}[\rho_g(r)] + \langle P_{nl}^g(r) \rangle + \langle E_{nl}^g(r) \rangle , \quad (29)$$

which should be compared with (14d). The pseudopotential hence becomes

$$W_{nl}^{g,PS}(r) = U_{nl}^{g}(r) + W_{tot}[\rho_{g}(r)] - W_{nl}^{g,v}[n_{g}(r)], \quad (30)$$

where the valence field is given by

$$W_{nl}^{gv}[n_{g}(r)] = -Z_{v}/r + W_{coul}[n_{g}(r)] + W_{xc}[n_{g}(r)],$$
(31)

which takes a similar form to the HF effective potential in (17). The  $U_{nl}^{g}(r)$  term is defined as in (16), but, of course, LDF  $\psi$ 's rather than HF  $\psi$ 's are to be used. Alternatively, we could derive (26) and (28), by setting an expression for the total energy of the fictitious atom in an external field  $W_{ext}(r)$ , of the type (18), and follow the Kohn and Sham variational treatment, to yield the effective single-particle equation for that system. Note that in deriving (30), no localization of any of the functionals is necessary [as is the case in the analogous HF pseudopotentials, eq. (14)] since  $W_{xc}[n]$  and  $W_{tot}[n]$  are local from the start. Again, eq. (26) with the potentials (30) is identically satisfied for the chosen reference state g of the atom, and the possible usefulness of this approach relies on the extent to which the core electrons in an *arbitrary* system can be replaced by (30). The pseudopotential (30) has been computed for several atoms [28] and tested by solving (26) self-consistently for electronic states other than g, yielding an accuracy of order  $10^{-3}$  au for eigenvalues and total energy differences for an excitation energy range of 8–17 eV.

### 4. Comparison of HF and LDF pseudopotentials

To elucidate the differences between the HF and the LDF pseudopotential and discuss the various underlying approximations related to their use for states other than the reference state g, we first examine the various terms entering the corresponding potentials in (17) and (30).

The form of the  $U_{nl}^{g}(r)$  term (16) is identical in both the HF and the LDF pseudopotentials. For pseudo-orbitals  $\varphi_{nl}^{g}$  with l that does not appear in the core (and n restricted to the ground state valence shell, e.g., 2p, 3d for first row atoms), there is no need to mix core orbitals  $\psi_{nl}^{g,c}$  in (6) to obtain a nodeless  $\varphi_{nl}^{g}$ since  $\psi_{nl}^{g,v}$  is already nodeless, and hence  $\varphi_{nl}^{g} = \psi_{nl}^{g,v}(r)$ and  $U_{nl}^{g}(r)$  is identically zero for all r. For orbitals with *l* components present in the core,  $C_{nl,n'l}^g \neq 0$ . Several limiting cases can be realized. If one chooses as  $\varphi_{nl}^{g}$  the true valence orbital  $\psi_{nl}^{g,v}$ , (i.e.,  $C_{nl,n'l}^{g}$  =  $\delta_{nl,n'l}$ ,  $U_{nl}^{g}(r)$  is again identically zero (note that even if  $\Phi_{nl}^{g}$  includes a radial node, as is the case for  $\Phi_{nl}^{g} =$  $\psi_{nl}^{g,v}$ , still  $\nabla^2 \varphi_{nl} / \varphi_{nl}$  can be nodeless) while if a single core orbital  $\psi_{nl}^{gc}$  is chosen to represent  $\varphi_{nl}^{g}$  (e.g., the nodeless 1s), then (15) reduces to

$$U_{nl}^{g}(r) \propto (\epsilon_{ni}^{g,v} - \epsilon_{nl}^{g,v}) |nl\rangle \langle nl|$$
(32)

(where the projector indicates that  $U_{nl}^{E}(r)$  operates only on the *ill* orbital) which has the Phillips--Kleinman [10] form. Both these choices assure of course that the eigenvalue problem (3) and (26) would yield the correct spectrum  $\epsilon_{nl}^{E,v}$  and reproduce the chosen orbitals (6), but the resulting effective potential  $V_{nl}^{g,eff}(r)$  in (8) and (26) might have "unphysical" features (e.g., in the second choice leading to (32), the effective potential does not approach zero at large r, but a constant value of  $\epsilon_{nl}^{g,v} - \epsilon_{nl}^{g,c}$ ). In general, only if there exists some radius  $R_c$ , such that for  $r > R_c$  all core orbitals entering the construction of  $\varphi_{nl}^{g}$  in (6) have essentially zero amplitude, while  $\psi_{nl}^{g,v}$  is still non-zero, then,  $\lim_{r\to\infty} U_{nl}^{g}(r) = \epsilon_{nl}^{gv} - \epsilon_{nl}^{gv''=0}$ . Otherwise,  $U_{nl}^{g}(r)$  and hence  $V_{nl}^{geff}(r)$  would have a non-zero value at infinity <sup>‡</sup>. Any "legitimate" choice of the pseudoorbitals in (6) leads (for l components present in the core) to a  $U_{nl}^{g}(r)$  that is strongly repulsive at small r, and decays very rapidly to zero (much faster than the valence orbitals themselves, due to cancellation with the denominator for  $r > R_c$ ). In particular, if  $\varphi_{nl}^{g}$  in (6) is chosen such that it has zero amplitude at the origin  $\varphi_{nl}^{g}(0) = 0$ , the  $U_{nl}^{g}(r)$  term would have a strong repulsive character at small r (for l not present in the core):

$$\lim_{r \to 0} U_{nl}^{g}(r) \propto (2l+3)/r^2 + O(1/r) + \dots, \qquad (33)$$

and would be zero everywhere for other l values. Since HF and LDF atomic orbitals are rather similar and since  $U_{p_1}^g(r)$  obeys (33) in both cases, one might expect that the HF and LDF derived  $U_{nl}^{g}(r)$  would be similar. Note particularly that [16,48], the short range repulsive character of  $V_{nl}^{g,eff}(r)$  is not needed to prevent a variational "collapse" of the valence pseudo-orbitals having the same l as some core state into the core. Any choice of  $\varphi_{nl}^{g}$  that does not satisfy  $\varphi_{nl}^g(0) = 0$  (i.e., mixing in (6) more core character than needed to remove the nodes of  $\psi_{nl}^{g,v}$ , or even the choice leading to (32), may give a non-repulsive  $U_{nl}^{g}(r)$ , but still yield the correct valence eigenvalues. One notes, however, that the choice  $\varphi_{nl}^{g}(0) = 0$  usually yields the maximum possible similarity between  $\varphi_{nl}^{g}(\mathbf{r})$ and  $\psi_{nl}^{g,v}(r)$  in the chemically important tail region. Any mixture of core character into  $\varphi_{nl}^{g}$ , more than required to remove the nodes from  $\psi_{nl}^{g,v}$  (which is required to avoid unphysical singularities in (16) at  $r \neq 0$ ) would reduce the possible similarity between  $\varphi_{nl}^{g}$  and  $\psi_{nl}^{gv}$  and would hence make the discussion of

bonding characteristics in molecules (and other valence properties related to  $\varphi_{nl}^{g}$  in terms of the pseudowavefunctions, less meaningful. Similarly, if the core mixing coefficients  $C_{nl,n'l}^{g}$  for n'l = core levels, are not minimized,  $\varphi_{nl}^{g}$  might have wiggles at small r that necessitate more plane waves or more atomic-like basis functions in linear expansion techniques [49]. In addition, the core region behavior of the pseudowavefunction would be unsatisfactory: too much mixing of core into the defining pseudo-orbital will lead to too little repulsion in the pseudopotential at small radius, and, as expected, too large a core contribution in all resulting valence functions. (Note that this repulsive character evolves from the fact that the core and valence orbitals have regions of mutual overlap; if this were not the case, (16) would reduce to a constant  $\sum_{n'}^{c} \epsilon_{n'}^{g,c}$ .) We conclude that if an accurate representation of the pseudowavefunctions (and not only eigenvalues) in the valence region is sought,  $U_{nl}^{g}(r)$  tends to be strongly repulsive in the core region.

Note that the  $U_{nl}^{g}$  term is largely confined to the core region: for  $r > R_{c}$  all  $R_{nl}^{g_{l}c}$  usually have small amplitudes and only the single term  $-C_{nl,nl}^{g}R_{nl}^{g_{l}v}\epsilon_{nl}^{g_{l}v}/C_{nl,nl}^{g}R_{nl}^{g_{l}v}$  survives from the second term of (16). This, in turn, tends to cancel against the first  $\epsilon_{nl}^{g_{l}v}$  term for large r, leaving a rapidly decaying  $U_{nl}^{g}(r)$  in this region.

Before passing to the discussion of the other pseudopotential terms, we briefly comment on the implications of this repulsive character on the Fourier representation of the pseudopotential. Clearly, the repulsive  $r^{-2}$  dependence of  $U_{nl}^{g}(r)$  at small r, overweights the attractive  $-r^{-1}$  dependence of the coulombic terms near the core, leading to sharply localized features of  $V_{nl}^{g,PS}(r)$  at small r, or alternatively, to a long tail in its Fourier representation  $V_{nl}^{g, PS}(q)$  in momentum space [28]. Numerous applications of empirical pseudopotentials to the optical properties of solids [7,50] have indicated that a "folding in" procedure of the plane wave representation of the pseudohamiltonian results in an effective potential that requires only relatively few *q* components (e.g.,  $q^2 = (h^2 + k^2 + l^2) \leq 12$ , where h, k, and l are the Miller indices of the reciprocal lattice vector) for an adequate representation of the low energy ( $\leq 10 \text{ eV}$ ) spectra of group IV and III-V. semiconductors. We note here that in terms of both the HF and the LDF first-principle pseudopotentials, this implies the relaxation of the  $\varphi_{p_i}^g(0) = 0$  (i.e., maximum orbital similarity) requirement and hence a reduc-

<sup>&</sup>lt;sup>‡</sup> This suggests that for a tightly bound valence orbital which has amplitude similar to that of a core state (e.g., f-electrons in rare earth elements) one would have to modify the definition of the core to include only shorter range orbitals.



Fig. 1. (a) Local density pseudo 2s orbital of carbon obtained by allowing extra 5% admixture of 1s character. (b) The "maximum similarity" pseudo 2s orbital of carbon, in which the core character is minimized.



Fig. 2. Local density s pseudopotentials for carbon (displayed as r times the pseudopotential). —— "maximum similarity" pseudo-orbital. --20% extra core mixture.

tion in the accuracy of the representation of the wavefunction in the valence region. To test how severe this trade-off might be, we have regenerated the carbon LDF pseudopotential, allowing some extra 5% mixture of  $\psi_{15}^{\text{pc}}$  into the  $\varphi_{5}^{\text{g}}$ . Solving for the ground state selfconsistently with this pseudopotential, we get the wavefunction depicted in fig. 1 (note the wiggle at small r, not present in the exact pseudowavefunction). The moments of  $r(\langle r^{\lambda} \rangle)$ , for  $-1 \leq \lambda \leq 3$  deviate from the exact pseudopotential results by 5.4%, 1.6%, 2.2% and 2.4% for  $\lambda = -1$ , 1, 2 and 3, respectively. If an extra 20% admixture of  $\psi_{1s}^{g,c}$  is permitted, the potential, as shown in fig. 2 can actually become attractive near the origin. As explained above, this will not affect the eigenvalue, but may very badly distort the value of wavefunction-related observables. The pseudopotential with extra  $\psi_{1s}$  lacks the  $r^{-2}$  dependence of  $U_{nl}^{g}(r)$  and consequently has a considerably shorter range Fourier representation (fig. 3). It hence appears that a moderate supression of the strongly repulsive "spike" in the pseudopotential does lead to a more convenient potential for use in reciprocal space techniques, without too much loss in the accuracy of the wavefunction representation.

The second term in (17),  $\langle V_{nl}^{g,tot}(r) \rangle$ , can be interpreted as a weighted average of the HF potential over



Fig. 3. Fourier components of the local density effective spotential of carbon, in units of the atomic volume ( $\Omega = 38.1$ au [7]). The momentum is measured in units of twice the Fermi wave vector for carbon ( $2k_F = 2.9188$  au [7]). --20% extra core character in the pseudo-orbital. — "maximum similarity" pseudo-orbitals.

the all-electron orbitals defining the pseudo-orbitals  $\varphi_{nl}^{g}$ , the weights being the orbital mixing coefficients  $C_{nl,n'l}^{g}$ . Note that while the Coulomb potential  $J_{n'l}^{g}(r)$  [eq. (3)] entering  $V_{n'l}^{g,tot}$  is local, the exchange terms  $K_{r'}^{g}(r)$  [eq. (4)] depend on the state on which they operate. The potential  $\langle V_{nl}^{g,tot}(r) \rangle$  can hence be interpreted as arising from a localization scheme such as  $\langle K_{nl'}^{g} \rangle = K_{nl'}^{g} \psi_{nl}(r) / \psi_{nl}(r)$ , where the localization subspace is just that determining pseudo-orbital  $\varphi_{nl}^{g}$ , in much the same way as the HF exchange potential is localized within a plane wave space to produce the local exchange functional [38, p. 21]. The analog of the  $\langle V_{nl}^{g,tot}(r) \rangle$  term in the local density pseudopotential theory [eq. (30)] is  $W_{tot}[\rho_g(r)]$ , where  $\rho_g(r)$  is the all-electron charge density and  $W_{tot}$  is the total LDF potential (Coulomb plus exchange correlation of core and valence). There is an important difference between the two: while  $\langle V_{nl}^{g,tot}(r) \rangle$  depends on the particular pseudo-orbital in question (and is hence *l*-dependent),  $W_{tot}[\rho_{g}(r)]$  is *l*-independent, since this operator, unlike the HF exchange, is local and hence factors out of the corresponding sums in eqs. (14a)-(14b). This implies that for all *l*-components not present in the core, the HF pseudopotential is still *l*-dependent (i.e.,  $V_{2p}^{g,PS} \neq V_{3d}^{g,PS}$ , etc. for first row atoms) while the LDF pseudopotential for I not present in the core is l-independent. In practice, one notes however [16,51], that the *l*-dependence of  $\langle V_{nl}^{g,tot} \rangle$  for the lowest *l* states not present in the core, is rather weak, and can usually be ignored. This simply results from the fact that in many cases, all the  $\psi_{nl}^{g,v}$  for the lowest *l* states not present in the core are spatially rather similar (e.g., 2p and 3d for first row atoms, having no nodes and obeying  $\psi_{nl}^{g,v}(0) = 0$ ) and hence lead to similar  $K_{nl}^{g,v}\psi_{nl}^{g,v}$  values (4)<sup>‡</sup>.

A further difference between the LDF total potential  $W_{tot}[\rho(r)]$  and the HF "averaged" total potential  $\langle V_{nl}^{g,tot} \rangle$  arises from their limiting behavior at large r since the LDF hamiltonian (20) does not provide complete cancellation between the Coulomb and exchange-correlation self-interaction [40;38, p. 21] the electron-nuclear and the electron-electron Coulomb potentials tend to cancel one another at large r, leaving the (exponentially decaying) exchange correlation tail. The HF potential, on the other hand, does decay asymptotically to the correct electrostatic value -(1+Q)/r, where Q is the net atomic charge. This fundamental difference leads to the well known discrepancies between HF and LDF energy, eigenvalues (i.e., the non-existence of Koopmans' theorem in LDF [38, p. 21]). At small r, both  $W_{tot}[\rho(r)]$  and  $\langle V_{nl}^{g,tot} \rangle$ decay to the -Z/r value.

Consider now the sum of the terms  $U_{nl}^{g}(r) + \langle V_{nl}^{g}t^{\text{ot}} \rangle$ and  $U_{nl}^{g}(r) + W_{tot}[\rho_{g}(r)]$  appearing in the HF and LDF pseudopotentials, respectively. This is the total effective potential for the ground state, eq. (8). The repulsive character of  $U_{nl}^{g}(r)$  in the core region would tend to cancel the all-electron Coulomb attraction, leaving a net "weak" potential. By "weak" we mean here simply that  $U_{nl}^{g}(r) + W_{tot}[\rho_{g}(r)]$  (or the corresponding HF term) would have fewer bound states than the original potential  $W_{tot}[\rho_{g}(r)]$ , which has core states as its lowest lying solutions [52]. This is just another way of displaying the "pseudopotential cancellation theorem" [39]. It is noted however that for "maximum similarity" choices of the pseudo-orbitals in (6) (e.g.,  $\varphi_{nl}^{g}(0) = 0$ ), the repulsive character of  $U_{nl}^{g}(r)$  over-

<sup>‡</sup> However, for larger l values, the centrifugal barrier  $\frac{1}{2}l(l+1)/r^2$ appearing in the all-electron hamiltonian (5) might localize the high l orbitals and lead to more substantial differences (e.g., d versus f orbitals). Thus we might expect the approximation made in many applications (15)–(25) of HF pseudopotentials, that the pseudopotential (17) is constant for all l not present in the core to break down for sufficiently high l. weights the attractiveness of  $W_{tot}[\rho(r)]$ , or even that combined with  $W_{nl}^{g,v}$ , leading to a net result that is "weak" in the sense of Heine [52] above, but not "weak" in the perturbative sense (e.g., might have a slowly convergent plane wave representation). Obviously, for *l* components not present in the core,  $U_{nl}^{g}(r) \equiv 0$  and the electron feels the full potential, with no cancellation. Hence, the p effective potential [eq. (8)] for the ground state g of a first-row atom has the form

$$V_{2p}^{g,eff} = W_{tot}[\rho_g(r)] + \frac{1}{2}l(l+1)/r^2$$
,

while the s effective potential is

$$V_{2s}^{g,eff} = W_{tot}[\rho_g(r)] + U_{nI}^g(r)$$

The  $U_{nl}^{g}(r)$  term is hence seen to replace the angular centrifugal barrier present for  $l \neq 0$ , and indeed  $V_{2p}^{g,eff}$  with this angular centrifugal potential added, resembles the 2s effective potential [10].

Finally, the last pseudopotential term  $W_{nl}^{g,v}[n(r)]$ or  $\langle V_{nl}^{g,v}(r) \rangle$  in LDF and HF, respectively, represents the field of the valence electrons in the presence of the external potential. At small *r* they both decay to  $-Z_v/r$  while at large *r*, the HF field decays to -(1+Q)/r, and the LDF field decays exponentially. Note however that the difference

$$W_{\text{tot}}[\rho(r)] - W_{nl}^{g,v}[n(r)] = -Z_c/r + \{W_{\text{coul}}[\rho(r)] - W_{\text{coul}}[n(r)]\} + \{W_{\text{xc}}[\rho(r)] - W_{\text{xc}}[n(r)]\}, \qquad (34)$$

would asymptotically decay approximately as  $W_{xc}[\rho(r)] - W_{xc}[n(r)]$ , Coulomb effects being already smaller at large r, and hence the spurious long range behavior of the total LDF potential would disappear in the LDF pseudopotential to the extent that  $\rho(r)$  and n(r) are similar in the tail region (which is usually the case, by construction, cf. (6)). Since, at small r, both (34) and the corresponding HF expression decay as  $-Z_c/r$  and since we have already argued that  $U_{nl}^g(r)$  is similar in the HF and LDF case, one might expect that the HF and LDF pseudopotentials would be rather similar in the entire range both due to the localization of  $\langle V_{nl}^{g,tot}(r) \rangle$  in the HF case, and due to the tail cancellation in the LDF case.

due to the tail cancellation in the LDF case. Figs. 4 and 5 show  $V_{2s}^{g,PS}$  and  $W_{2s}^{g,PS}$  and  $V_{2p}^{g,PS}$  and  $W_{2p}^{g,PS}$  for the ground state g of carbon, respectively, where the HF results are taken from Kahn et al. [16].



Fig. 4. Hartree–Fock (---) and local density (---) s-pseudopotentials for carbon. Note the cut-off at  $rV \le 10$  e.



Fig. 5. Hartree-Fock (---) and local density (----) p-pseudopotentials for carbon.

It is clear that within the employed scale, they are indeed indistinguishable. To further test this point, we

# Table 1

Energy eigenvalues and orbital moments for carbon obtained in: (a) exact all-electron LDF calculation, (b) LDF calculation with LDF pseudopotentials, (c) LDF calculation with HF pseudopotential of ref. [16]. Energy in atomic units and moments of r in the corresponding bohr radii units. Superscript "0" denotes the  $1s^22s^22p^2$  ground state and "\*" denotes the  $1s^22s^12p^3$  excited state

	(a) exact LDF	(b) LDF pseudo LDF calculation	(c) HF pseudo LDF calculation
orbital energy			
e2s	-0.45738	-0.45738	-0.45688
€2D	-0.15795	-0.15795	-0.15632
$\epsilon_{2S}^{*}$	0.47448	-0.47265	-0.47728
€2p	-0.17344	-0.17556	-0.173821
orbital moments			
$(r^{-2})_{2S}^{0}$	3.54994	0.82143	0.80642
$(r^{-1})_{2S}^{0}$	0.91358	0.79909	0.79364
(r <sup>1</sup> ) <sup>0</sup> <sub>25</sub>	1.59383	1.56258	1.56845
$\langle r^2 \rangle_{2S}^0$	3.08962	2.97877	2.99561
$(r^{-2})_{2S}^{*}$	3.58021	0.82931	0.82106
(r <sup>-1</sup> ) <sup>*</sup> <sub>25</sub>	0.91777	0.80350	0.79931
$\langle r^1 \rangle_{2S}^*$	1.58557	1.55143	1.55161
$\langle r^2 \rangle_{2S}^*$	3.05354	2.93134	2.94331

have solved the LDF pseudopotential equation (26) for the ground and the  $2s^{1}2p^{3}$  states of carbon, replacing the LDF pseudopotential  $W_{nl}^{g,PS}(r)$ , by the HF pseudopotential  $V_{nl}^{g,PS}(r)$  of Kahn et al. The results are shown in table 1, where they are compared with those obtained with  $W_{nl}^{g,PS}(r)$  and from the direct solution of the all-electron LDF equation (19). It is clear that not only are the eigenvalues obtained with these pseudopotentials very close, but also the wavefunctions are well reproduced (as they should be since the  $C_{nl,n'l}$  were chosēn in the same way).

We close this section by a note on the "core-like" character of the pseudopotentials derived here. We have indicated already that  $V_{nl}^{\rm g,eff}(r)$  and  $W_{nl}^{\rm g,eff}(r)$  are largely confined to the core space and that they correspond to an effective field of an  $N_{\rm c}$ -electron system in that the last two terms in the corresponding expressions (17) and (30) [cf. cq. (34)] contain a difference between an all-electron and a valence field. This does

not indicate however that these pseudopotentials represent a bare-ion [7,53-57] (i.e., core) effective field. The last two terms in (17) and (30) give rise to direct core-valence interaction terms due to both the non-linearity of the LDF exchange-correlation functional (i.e.,  $W_{xc}[\rho_c + \rho_v] \neq W_{xc}[\rho_c] + W_{xc}[\rho_v]$ ) and the state dependence of the HF exchange (i.e., the explicit omission of the self-exchange terms results in  $\langle V_{nl}^{g,tot}(r) \rangle - \langle V_{nl}^{g,v}(r) \rangle \neq \langle V_{nl}^{g,c}(r) \rangle$ . Rather, these pseudopotentials replace the core field in the presence of the actual valence-valence and core-valence interactions in the reference electronic state g. This should be contrasted with the widely used model "ionic pseudopotentials" developed by Heine and co-workers [53,54] and the local density pseudopotentials used by Cohen and co-workers [56,57]. In these models one actually uses for the pseudopotential  $V_{nl}^{g,PS}$  a field generated from the bare ion core (e.g., Si4+, Nb5+) with no valence electrons, and applies it directly to systems including a complete valence manifold (e.g., Si<sup>0</sup> and Nb<sup>0</sup>). In practice, the bare ion pseudopotential is usually generated by assuming an analytic form either in direct [53-55] or in momentum [56, 57] space with suitable asymptotic behavior, and fixing the adjustable parameter of the forms to reproduce the observed one-electron excitations of the corresponding single valence electron systems (e.g., Si<sup>3+</sup>, Nb4+). Once the bare pseudopotential is fixed,  $V_{m}^{g,eff}(r)$  [eq. (8)] is constructed by either adding to  $V_{nl}^{g,pS}(r)$  a dielectrically screened free-electron field with a position independent valence exchange correlation energy [54], or a Kohn-Sham valence field [55-57] with pure exchange only. If one is to take up the first principles HF or LDF pseudopotential approach as a starting point, as we have done here, the bare-ion approach implies:

(a) linearization of the LDF exchange-correlation functionals with respect to the core and valence densities, (e.g., core-valence non-penetrability approximation [39]), or, alternatively, assuming that the valence and core orbitals are solutions to the same Fock operator; (b) replacement of the valence part of the charge density  $\rho(r)$  which includes radial nodes by the pseudocharge density; this is referred to in a slightly different context, as neglect of the "orthogonality hole" [52, 58];

(c) approximating the neutral atom core orbitals determining the Coulomb and exchange parts of the core field [eq. (34)] by those pertaining to a bare ion (i.e., neglect of core relaxation in going from  $Si^{4+}$ , Nb<sup>5+</sup> to Si and Nb).

Some previous documentation of these approximations in a different context, for example, approximating the core Fock operator for a single valence electron system by a valence Fock operator [49], neglect of corevalence interference terms in linearized versions of the LDF exchange [59] or neglect of orthogonality hole in molecular calculations [27] indicates that their effect, relative to the non-approximated first principles results, might be rather severe. As a simple test, we solve eq. (26) for the ground state g of oxygen atom, where the pseudopotential  $W_{RI}^{PS}(r)$  is approximated by a "bare ion" form. We first assume linearization (a) but not a neglect of the orthogonality hole (b) or the core relaxation (c):

$$W_{nl}^{g,PS}(r) \approx U_{nl}^{g}(r) + \{-Z_{c}/r + W_{coul}[\rho_{c}(r)] + W_{xc}[\rho_{c}(r)]\} + \{W_{coul}[\rho_{v}(r)] - W_{coul}[n(r)]\} + \{W_{xc}[\rho_{v}(r)] - W_{xc}[n(r)]\}, \qquad (35)$$

where  $\rho_v$  and  $\rho_c$  denote real valence and core densities, respectively. The error in the 2s and 2p eigenvalues is 0.43 eV and 0.5 eV, respectively, relative to the correct form of  $W_{nl}^{g,PS}(r)$  in eq. (30) which satisfies (26) for the ground state as an identity. We next neglect the orthogonality hole in both the Coulomb and the exchange correlation part by discarding the last two curly brackets in (35). The errors in the 2s and 2p eigenvalues are now 0.44 eV and 0.51 eV, respectively, here, the neglect of the orthogonality correction in the interelectronic (repulsive) Coulomb potential is partially compensated by the similar neglect in the (attractive) exchange correlation potential. Finally, we neglect core relaxation by using for  $\rho_c$  in (35) the core density of a O6+ ion. This yields errors of 0.85 eV and 0.95 eV in the 2s and 2p eigenvalues, respectively. Clearly, a bare ion approach to the first principle LDF pseudopotential does not work, and some suitable empirical or theoretical parametrization of the pseudopotential is needed in order to obtain sensible results. Such an empirical parametrization, when carried out in the framework of a local density screening field [55-57], gives rise to an additional theoretical difficulty. The LDF energy eigenvalues do not corre-

spond to actual elementary excitations, not only because of the neglect of orbital relaxation effects [38, p. 43] (i.e., the inaccuracy in the approximation underlying Koopmans' theorem, namely that the orbitals involved in the excitation process do not relax spatially, relative to the ground state orbitals, due to the hole formation), and the lack of "complete" electronelectron correlation terms in the approximate forms of the LDF functionals (i.e., neglect of correlation self-energy [60]), but also because Koopmans' theorem does not apply to this hamiltonian [32;38, p. 21] in some cases, even to extended system [32]. This stems from the well known non-cancellation between the Coulomb and exchange self-interaction terms [38, p. 21]. This difficulty can be partially circumvented by using total energy, rather than eigenvalue differences, (" $\Delta$ SCF" model [32,61]) to approximate the actual excitation energy, in which case, self-interaction cancellation as well as relaxation effects are properly accounted for. Previous experience with this approach using either a complete  $\triangle$ SCF [32], or an approximate "transition state" model [62] has indicated that the correction to the eigenvalue difference, necessary to bring it into agreement with the correct theoretical excitation energy, (which is close to the observed values) is strongly state dependent. An empirical parametrization of the bare ion pseudopotential, designed to yield eigenvalues that match the observed excitation energies in extended systems via an LDF screening function, thus has to compensate not only for the deficiencies mentioned in the text, but also for this state dependence (not only I-dependence) of the calculated excitation energies. Numerous attempts in this direction [55-57] have shown that this goal can apparently be achieved with moderate success for certain energy ranges in polyatomic systems. Still, the theoretical difficulties mentioned here remain largely unresolved and call for a better understanding of the success of these procedures for predicting energetics, as well as their implication on the quality of the resulting wavefunctions.]

# 5. Use of pseudopotentials for arbitrary states

We have shown so far that the original HF and LDF equations for an atom in electronic state g can be rigorously transformed to the pseudohamiltonian equations (7) and (26) having the same eigenvalues but wavefunctions given by (6) instead of the original nodal  $\psi_{nl}^{g,v}$ . We now inquire whether the same pseudopotential  $V_{nl}^{g,PS}$  and  $W_{nl}^{g,PS}$  can be used to replace the core electrons for states other than g and for atoms in an arbitrary bonding configuration.

# 5.1. Angular momentum dependence

The analysis of the terms appearing in the pseudopotentials (17) and (30) has indicated a strong *l*-dependence: the Pauli principle manifests itself in real space oy requiring a repulsive  $U_{nl}^{g}(r)$  for *l*-components present in the core and a vanishing  $U_{nl}^{g}(r)$  for *l* components not present in the core. An additional weak *l*-dependence appears in the HF pseudopotential term  $\langle V_{nl}^{g,tot}(r) \rangle$  [eq. (14a)] due to the nonlocality of the HF exchange. Hence, when applied to an arbitrary system,  $V_{nl}^{g,PS}$  and  $W_{nl}^{g,PS}$  operate on individual *l*-components of given atomic sites. This can be written formally as

$$V_{\alpha}^{g,PS}(r-R_a) = \sum_{lm}^{\infty} V_{nl}^{g,PS}(r-R_a) |lm\rangle_a \langle lm|_a , \qquad (36)$$

where  $|Im\rangle_a$  indicates angular momentum projectors on site a and  $V_{\alpha}^{g,PS}(r-R_a)$  is the total pseudopotential of atom of type  $\alpha$  replacing the core electrons on this site. Obviously, had we solved a non-central field atomic equation instead of the approximately spherically averaged forms (5) and (19), we would have obtained a vector pseudopotential with explicit *m*-dependence. Similarly, a spin-polarized version of (5) and (19) or a relativistic version would have resulted in additional spin and wavefunction components (minor and major) dependence and the corresponding projectors in (36). These are however considered as extensions of the simple theory of sections 2 and 3 and would not concern us here.

Eq. (36) indicates the type of trade-off involved in using the pseudopotential; while the original LDF allelectron equation is characterized by a state independent hamiltonian (and hence all wavefunctions are solutions to a single operator), the solution of the pseudohamiltonian involves a different operator (30) for the *I*-components present in the core than from those not present in the core. The number of important *I*-components in (36) is just the number of angular momenta required to represent the particular wavefunction of interest, and for most energy regions in molecules and solids this can be truncated to a fairly small number ( $l \le 3$ ) [16,35]. Furthermore, the sum in eq. (36) can be rather easily extended to a high limit by replacing the pseudopotential of the high *l*-components not present in the core, by that of the lowest one; as shown in section 4, this is exact for the LDF pseudopotential and a good approximation for the HF pseudopotentials [16,51].

### 5.2. Frozen core approximation

The replacement of the effect of core electrons by a pseudopotential calculated from the orbitals of a chosen reference electronic state g implies "freezing" these core orbitals in the system under consideration at the level g. Consideration of any observable that is related to the modification of the core in an actual system relative to a ground state atom, such as core polarization in rare earth, Knight shifts or Fermi contact interactions, would generally require an explicit all-electron solution, although reorthogonalization to the new valence field may produce a reasonable approximation [28]. The effect of the frozen core approximation on "valence properties" is usually small and can frequently be neglected [16,36,63]. The essential approximation here is that we replace the actual valence-valence interaction  $V_{nl}^{g,v}$  in eq. (5) and (19) in the presence of the dynamic core potential  $V_{nl}^{g,c}$ , by an interaction having the same form but added to a static external potential which is fixed at a given electronic reference state of the atom. This external potential is constructed from the actual core + valence solutions at state g, and is "frozen" at that level when applied to an arbitrary state  $e \neq g$ . We note that contrary to the methods that construct the pseudopotential from a single valence electron ion [55-57, 64] (e.g.,  $C^{3+}$ ,  $Al^{2+}$ ,  $O^{5+}$ ) and then apply it to polyatomic systems made of neutral atoms, where the valence-valence interactions are computed from *pseudo* rather than true orbitals, the method described in this paper uses the exact valence-valence interactions in the neutral system held in the reference state g to describe the pseudopotential. The reference state can be chosen to be sufficiently close to that pertaining to the polyatomic systems of interest (e.g., sp<sup>3</sup> atoms to be used in tetrahedrally bonded systems) so

that the core orbitals are frozen in a state that resembles that of the system under consideration.

# 5.3. Energy dependence

We have chosen to construct the pseudopotential, by inverting an atomic one-particle equation of the form (5) or (19). In fact, there is no special reason to construct this potential from a system having solutions that decay to zero at infinity; since the pseudopotential is going to be used to replace core electrons in a polyatomic system, we might as well construct it from some other single-site eigenvalue problem such as that pertaining to an atom embedded in a spherically averaged potential field due to the other nuclei, a Wigner-Seitz sphere, a "renormalized atom" [65], etc. Since the boundary conditions on the wavefunction in these systems are different from those pertaining to an atom in free space (e.g., vanishing logarithmic derivative on some Wigner-Seitz boundary), the resulting central field orbitals and energies  $\{\psi_{nl}, \epsilon_{nl}\}$  would be different, and hence the pseudopotential would be different even within a given *l*-component. Similarly, one could have constructed an s potential for a first row atoms not only from the ground state 1s and 2s orbitals, but also from the 3s, 4s, ... orbitals or from some excited (1s 2s 2p) configurations (e.g.,  $1s^22s^12p^3$ ). In all these cases, a distinctly different s potential would be obtained. These are just different ways of stating that our pseudopotential is energy dependent (or, principal quantum number dependent) even for equal *I*. It is clear that such a pseudopotential is useful only to the extent that this energy dependence is weak, otherwise it will have to be reconstructed for different situations.

This energy dependence originates from two (related) sources: the energy dependence of the core orbitals to state g (which is usually very small and neglected in the frozen core approximation) and the modification of each of the *l*-components of the valence field. Consider the energy dependence of the pseudopotential that results from using different central-field solutions for its construction (e.g., varying g or changing the atomic boundary conditions). The difference in the corresponding pseudopotentials would be mostly confined to the core region, since  $U_{nl}^g(r)$  is non-zero only in this region (cf., section 4) and since the difference  $\langle V_{nl}^{g,tot}(r) \rangle - \langle V_{nl}^{g,v} \rangle$  or  $W_{tot}[\rho_g(r)] - W_n^{vg}[n(r)]$  between total and valence potentials reflects approximately a core field, where the localization of the HF exchange potential in  $\langle V_{n1}^{g,tot}(r) \rangle$  [eq. (14a)] weights mostly the core part of the valence potential. Hence, to the extent that the orbitals of states g1 and g2 are similar in the core region for each *l*-component, one would expect similar pseudopotentials, and conversely, any variation in these orbitals in the core region results in an energy dependence of the pseudopotential. In cases where the frozen core approximation is applicable, it is reasonable to assume that the resulting energy dependence would be small.

One can test this energy dependence in several simple ways: For instance, one can generate the pseudopotential from a reference electronic state g which has only certain principal quantum numbers occupied (e.g., ground state) and apply it to some excited states e having additional principal quantum numbers occupied (e.g.,  $2s^2 3s^2$ ,  $2s^2 4s^2$ , etc. in a first row atom). If we denote by  $\epsilon_{nl}^{v,e}$  the exact (all electron) eigenvalue in the electronic state e and by  $\epsilon_{nl}^{v,e}[g]$  the eigenvalue at the same state obtained by using the pseudopotential generated from the electronic state g, then the error  $\Delta \epsilon_{nl}^{v,e}[g] = \epsilon_{nl}^{v,e} - \epsilon_{nl}^{v,e}[g]$  forms a measure to the energy dependence of the pseudopotential. Table 2 shows  $\Delta \epsilon_{2s}^{v,e}[g], \Delta \epsilon_{3s}^{v,e}[g]$  and  $\Delta \epsilon_{4s}^{v,e}[g]$  for carbon, where g is the ground configuration  $1s^2 2s^2 2p^2$  and e is  $2s^2 2p^2$ ,  $2s^2 2p^0 3s^2$  and  $2s^2 2p^0 4s^2$ , respectively. The error is usually within  $< 10^{-2}$  au of the exact eigenvalue [28]. One can alternatively vary g and keep e constant, i.e., generate the pseudopotential from different configurations and test it on a given configuration e. Table 3 shows  $\Delta \epsilon_{2s}^{v,e}$  and  $\Delta \epsilon_{2p}^{v,e}$  for  $g = 1s^2 2s^2 2p^2$ ,  $1s^2 2s^1 2p^3$  and  $1s^2 2s^{1.5} 2p^{2.5}$ . Again, the errors  $\Delta \epsilon$ do not exceed  $\approx 10^{-5}$  au of the corresponding exact eigenvalues. We hence neglect the energy dependence of our pseudopotential  $V_{nl}^{\text{PS},g}(r)$  and drop the reference state index g and the principal quantum number index n. The total HF atomic pseudopotential for atom of type  $\alpha$  located at site *a* in the polyatomic system is hence given by

$$V_{\alpha}^{\rm PS}(r) = \sum_{lm}^{\infty} V_l^{\rm PS}(r) |lm\rangle_{\alpha} \langle lm|_{\alpha} . \qquad (37)$$

# Table 2

The error  $\Delta e_{\mu}^{\nu} e[g]$  in the energy eigenvalue  $\mu$ , obtained when the LDF pseudopotential generated from configuration  $g \equiv$  $1s^2 2s^2 2p^2$  in carbon, is applied to configuration e. Results in atomic units. The 3s and 4s states were obtained as "bound state" by placing the carbon atom in a potential well of depth -1.0 au and radius 10 au. The errors for  $e = g = 2s^2 2p^2$  reflect the numerical inaccuracies

Applied to configuration e	$\Delta \epsilon_{2S}^{v,e}[g]$	$\Delta \epsilon_{3S}^{V,e}[g]$	$\Delta \epsilon_{4S}^{\gamma,e}[g]$
	$\mu = 2s$	$\mu = 3s$	$\mu = 4s$
2s <sup>2</sup> 2p <sup>2</sup> 3s <sup>0</sup> 4s <sup>0</sup>	$7.0 \times 10^{-8}$	$5.0 \times 10^{-8}$	4.0 × 10 <sup>-8</sup>
2s <sup>2</sup> 3s <sup>2</sup> 4s <sup>0</sup>	$1.4 \times 10^{-4}$	1.0 × 10 <sup>-5</sup>	2.1 × 10 <sup>-5</sup>
2s <sup>2</sup> 3s <sup>0</sup> 4s <sup>2</sup>	$5.1 \times 10^{-3}$	6.2 × 10 <sup>-3</sup>	8.4 × 10 <sup>-3</sup>

### Table 3

The error  $\Delta e_{\mu}^{\mu} e_{\beta}^{\mu}$  [g] in the energy eigenvalue  $\mu$ , obtained when the LDF pseudopotential is generated from different configurations g and applied to the configuration  $e \equiv 1s^2 2s^2 2p^2$ . Results given in atomic units. See caption to table 2 for more details

Generated from configuration g	$\Delta \epsilon_{2s}^{v_{s}e}[g]$	$\Delta \epsilon_{2p}^{\mathbf{v},\mathbf{e}}[\mathbf{g}]$	$\Delta \epsilon_{3s}^{v_s} e[g]$
	$\mu = 2s$	$\mu = 2p$	$\mu = 3s$
1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>2</sup>	$7.0 \times 10^{-8}$	$1.0 \times 10^{-7}$	1.0 × 10 <sup>-5</sup>
1s <sup>2</sup> 2s <sup>1</sup> 2p <sup>3</sup>	$6.2 \times 10^{-8}$	3.1 × 10^{-7}	2.3 × 10 <sup>-5</sup>
1s <sup>2</sup> 2s <sup>1.5</sup> 2p <sup>2.5</sup>	$6.6 \times 10^{-8}$	2.2 × 10^{-7}	2.4 × 10 <sup>-5</sup>

# 5.4. Superposition approximation

In order to apply the atomic pseudopotential  $V_{\alpha}^{PS}(r-R_a)$  [eq. (37)] to polyatomic systems, we assume that the total effective potential is given by

$$V_{\text{tot}}^{\text{eff}} = V^{v} + V_{\text{tot}}^{\text{PS}},$$

$$V_{\text{tot}}^{\text{PS}} = \sum_{a} \sum_{\alpha} V_{\alpha}^{\text{PS}}(r - R_{a,\alpha}),$$
(38)

where  $V^{v}$  is the valence potential in the polyatomic system calculated utilizing the valence pseudo-orbitals, and the sum in the second term in (38) is extended over all atoms in the system of types  $\alpha$  at sites *a*. Here we have assumed that the atomic pseudopotentials  $V_{\alpha}^{PS}(r - R_{\alpha})$  can be superposed to yield an external field that replaces the core electrons in the polyatomic system. Clearly, if we were to apply the pseudopotential formalism directly to the polyatomic system, we would obtain a form that is not directly separable to

a linear superposition of atomic-like terms, due both to the non-spherical geometry and to non-linearity of the exchange in both HF and LDF approaches with respect to the tails extending from one site into the domain of another site, and hence (38) is an approximation. It seems difficult to assess the validity of the superposition approximation, not knowing the exact interference effects involved in a pseudopotential transformation pertaining to the polyatomic system. Some discussion of the non-additivity corrections has been presented by Animalu and Heine [54]. Molecular finite-basis HF calculation [16-26] reveal no serious errors arising from (38). Note, however, that in the approach presently used, we use only the transferability and additivity of the atomic pseudopotential  $V_{\alpha}^{PS}(r-R_a)$ and not of the effective atomic potential  $[V_{\alpha}^{PS}(r-R_a)+$  $V^{v}(r-R_{n})$ ], as used in some model potential approaches [7]. We hence only assume the additivity of the rather short range "core" potential, while the valence field  $V^{v}$  in the polyatomic system remains in the same form it had in the all-electron model (i.e., non-linear with respect to the contributions  $V^{v}(r-R_{n})$  coming from individual sites), and is allowed to adjust self-consistently, reflecting accurately the valence-valence interactions in the system of interest. Our analysis of section 4 indicates that the atomic pseudopotential  $V_{\alpha}^{\text{PS}}(r)$  is rather short-range. Due to both the rapid fall-off of  $U_l(r)$  and the tail cancellation in  $\langle V_{nl}^{g,tot}(\mathbf{r}) \rangle - \langle V_{nl}^{g,v} \rangle$  or  $W_{tot}[\rho_g(\mathbf{r})] - W_n^{g,v}[n(\mathbf{r})]$ , the resulting  $V_{\alpha}^{PS}(\mathbf{r})$  is even shorter range than the all-electron potentials  $V_{nl}^{g,tot}$  and  $W_{tot}[\rho_g(\mathbf{r})]$ , so that the interference between nearest neighbor pseudopotentials in (38) is minimal. For example, the carbon 1s pseudopotential is only 0.034 au at the distance from the origin corresponding to the bond center in diamond (compared with -0.865 au for the full potential).

The superposition assumption in (38) allows the use of simple forms for the matrix representation of the pseudopotential. If a plane wave basis set is used, such as

$$|K\rangle = e^{-i(k+G)r}; |K'\rangle = e^{-i(k+G')r},$$
 (39)

where k indicates the position in the Brillouin zone and G is a reciprocal lattice vector, then the matrix of the *total* pseudopotential  $V_{tot}^{PS}(r)$  [eq. (38)] is given by

$$\langle \mathbf{K} | \mathbf{V}_{\text{tot}}^{\text{PS}} | \mathbf{K}' \rangle = 4\pi \sum_{l,\alpha} (2l+1) P_l(\cos \theta_{\mathbf{K}\mathbf{K}'})$$
$$\times F_{l\alpha}(\mathbf{K}, \mathbf{K}') S^{\alpha}(\mathbf{G} - \mathbf{G}'), \qquad (40)$$
$$F_{l\alpha}(\mathbf{K}, \mathbf{K}') = \langle j_l(\mathbf{K}\mathbf{r}) | \mathbf{V}_l^{\text{PS}}(\mathbf{r}) | j_l(\mathbf{K}'\mathbf{r}) \rangle,$$

where  $P_I$  is the Legendre polynomial,  $j_I(Kr)$  are the spherical Bessel functions (here we used the standard expansion of a plane wave in terms of the Legendre polynomial and the Bessel function) and the structure factor  $S_{(G-G')}^{\alpha}$  for species  $\alpha$  is

$$S^{\alpha}(G-G') = \frac{1}{N} \sum_{R_a} e^{-i(G-G')R_{a,\alpha}}, \qquad (41)$$

where N is the number of atoms and  $R_{a,\alpha}$  denotes the position vector of species  $\alpha$  in cell a. The superposition model (38) in connection with a plane wave basis hence allows one to factor out the structural information for each sublattice into  $S^{\alpha}_{(G-G')}$  while the rest of the potential elements are given by the  $F_{l\alpha}(K, K')$  terms, which can be calculated by a one dimensional numerical integration for each atom.

#### • 5.5. Total energy

The calculation of the total electronic energy  $E_t$  of a polyatomic system in the HF pseudopotential scheme has been discussed by Kahn et al. [16], where it was shown the  $E_t$  can be partitioned into a core part not included in the pseudopotential scheme and a valence part. The two center contribution of the core part, which is geometry dependent, can either be calculated directly from the core densities or approximated by a simple asymptotic form, such as a screened nuclearnuclear term. In both cases, the quality of the computed equilibrium bond length is comparable to that obtained in the corresponding all-electron calculation. Since the same discussion applies to the LDF pseudopotential, it will not be repeated here. Instead, we will briefly mention another aspect of the LDF total energy in the pseudopotential scheme, namely the existence of the "transition state" concept.

One of the attractive features of the all-electron LDF theory is the fact that one can calculate, to within a good approximation, the total energy difference  $\Delta E_{ij}$  between an excited and a ground state system (" $\Delta$ SCF") by performing a single calculation on a system having its i and j occupation numbers halfway between that of the corresponding ground and excited states. This concept has been of great importance for computing binding and excitation energies for molecules [62] and solids [32] in that it allows a convenient way to introduce relaxation and self-interaction cancellation.

The fact that the LDF total energy [eqs. (24) and (27) is an analytic function of the orbital occupation numbers  $N_i$ , has been used by Slater [38, p. 43] to construct a Taylor series expansion of the total energy difference  $\Delta E_{ii}$  around a specific single point in the occupation number space, where all the odd terms in the occupation number differences vanish. To the extent that the second derivatives of the energy with respect to the sum of the ith and jth occupation numbers can be neglected, the total energy difference is simply given by the eigenvalue difference, computed with the specific occupation numbers, generally  $N_i =$  $N_i = \frac{1}{2}$ . Since only the density is effected by  $W_{ext}(r)$ , the total energy expression (24) does not depend explicitly on the external field and therefore the same argument can be carried for the energy expressed in terms of the pseudodensity n(r).

To demonstrate the applicability of the transition state concept to the LDF pseudopotential problem, we have calculated the all-electron total energy difference  $\Delta E_{ij}$  and the all-electron transition state eigenvalue difference  $\Delta \epsilon_{ij}^{\text{TS}}$ , as well as the corresponding quantities  $\Delta E_{ij}^{\text{PS}}$  and  $\Delta \epsilon_{ij}^{\text{TS,PS}}$  for the pseudopotential problem, for carbon (table 4). The quantity  $\Delta E_{ij} - \Delta \epsilon_{ij}^{\text{TS}}$ 

#### Table 4

Comparison of exact LDF total energy differences  $\Delta E_{ij}$  with pseudopotential total energy differences  $\Delta E_{ij}^{PS}$  for carbon. The corresponding transition state eigenvalue differences are denoted as  $\Delta \epsilon_{ij}^{TS}$  and  $\Delta \epsilon_{ij}^{TS,PS}$ . The quantity  $\Delta E_{ij} - \Delta \epsilon_{ij}$  measures the error in the transition state calculation for the allelectron LDF model, while  $\Delta E_{ij}^{PS} - \Delta \epsilon_{ij}^{PS}$  measures the similar error in the LDF pseudopotential model. Results are given in atomic units

Configuration	∆E <sub>ij</sub>	$\Delta E_{ij}^{\text{PS}}$	$\Delta E_{ij} - \Delta \epsilon_{ij}^{\text{TS}}$	$\Delta E_{ij}^{\mathrm{PS}} - \Delta \epsilon_{ij}^{\mathrm{TS,PS}}$
$2s^{2}2p^{2} \rightarrow 2s^{2}2p^{1}$	0.35802	0.35736	0.00543	0.00530
$\begin{array}{c} 2s^2 2p^2 \rightarrow \\ 2s^1 2p^2 \end{array}$	0.36021	0.35982	0.00421	0.00411

measures the accuracy of the transition state model in the exact all-electron calculation, while the numerical quantity  $(\Delta E_{ij} - \Delta \epsilon_{ij}^{\text{TS}}) - (\Delta E_{ij}^{\text{PS}} - \Delta \epsilon_{ij}^{\text{TS},\text{PS}})$ forms a measure for the extra error introduced by the pseudopotential scheme. These errors are indeed seen to be small, confirming the usefulness of the transition state method in the pseudopotential framework.

# 6. Relation to the Phillips-Kleinman scheme

Here we compare the angular momentum projected pseudopotentials with the Phillips-Kleinman (PK) [10] pseudopotential scheme. Phillips and Kleinman showed that since the valence orbitals  $\psi^{v}_{\mu}$  are orthogonal to the core functions  $\psi^{c}_{\mu}$ , one can display the valence solutions as

$$\psi^{\mathbf{v}}_{\mu} = \varphi^{\mathbf{v}}_{\mu} - \sum_{v}^{c} \langle \varphi^{\mathbf{v}}_{\mu} | \psi^{c}_{v} \rangle \psi^{c}_{v} , \qquad (42)$$

where  $\varphi_{\mu}^{\mathbf{v}}$  is an arbitrary valence-like function which does not have to be core orthogonal, and use  $\psi_{\mu}^{\mathbf{v}}$  in the valence eigenvalue problem

$$H^{\mathsf{v}}\psi^{\mathsf{v}}_{\mu} = \epsilon\psi^{\mathsf{v}}_{\mu} , \qquad (43)$$

to get

$$H^{\mathbf{v}}\varphi_{\mu}^{\mathbf{v}} - \sum_{v}^{\mathbf{c}} \langle \varphi_{\mu}^{\mathbf{v}} | \psi_{v}^{\mathbf{c}} \rangle H^{v} \psi_{v}^{\mathbf{c}} = \epsilon \varphi_{\mu}^{\mathbf{v}} - \epsilon \sum_{v}^{\mathbf{c}} \langle \varphi_{\mu}^{\mathbf{v}} | \psi_{v}^{\mathbf{c}} \rangle \psi_{v}^{\mathbf{c}} .$$

$$(44)$$

If one assumes that the core orbitals  $\psi_u^c$  are also eigenfunctions of the valence hamiltonian  $H^v$ , i.e.

$$H^{\mathsf{v}}\psi_{\mathsf{v}}^{\mathsf{c}} = \epsilon_{\mathsf{v}}^{\mathsf{c}}\psi_{\mathsf{v}}^{\mathsf{c}} \,, \tag{45}$$

then (42)-(44) yield

$$[H^{\mathsf{v}} + V_R^{(\mathsf{u})}(\epsilon, r)]\varphi_{\mu}^{\mathsf{v}} = \epsilon \varphi_{\mu}^{\mathsf{v}}$$
(46)

where the pseudopotential is given by

$$V_{R}^{(\mu)}(\epsilon,r) = \sum_{v}^{c} \left(\epsilon - \epsilon_{v}^{c}\right) \langle \varphi_{\mu}^{v} | \psi_{v}^{c} \rangle \psi_{v}^{v} / \varphi_{\mu}^{v} .$$
(47)

One has hence replaced the original valence equation (43) having core-orthogonal (and hence oscillatory) solutions  $\Psi^{\nu}_{\mu}$ , by a modified equation (46) having the same eigenvalue spectra but solutions of the form

$$\varphi_{\mu}^{\rm v} = \psi_{\mu}^{\rm v} + \sum_{v}^{\rm c} a_{\mu v} \psi_{v}^{\rm c} , \qquad (48)$$

with arbitrary core components in them. Note, however, that condition (45) is not met in general: in the HF scheme, (45) applies only to bare ions having a closed shell with no valence electrons, in which case  $G(\{\Psi_{\mu}^{v}\})$  in (7) is zero, while in systems with valence electrons, (45)–(46) is incorrect.

In many studies using the PK formalism, the valence field was neglected. For a single valence electron outside a closed shell core, the valence Fock-hamiltonian is

$$H^{v} = -\frac{1}{2}\nabla^{2} - Z/r + \sum_{v}^{c} 2J_{v}^{g,c} - K_{v}^{g,c}, \qquad (49)$$

and the core hamiltonian

$$H^{c} \approx -\frac{1}{2} \nabla^{2} - Z/r + \sum_{v}^{c} 2J_{v}^{g,c} - K_{v}^{g,c} + J^{g,v} - \frac{1}{2} K^{g,v}.$$
(50)

This was approximated by .

$$H^{c} \approx H^{v}$$
, (51)

which is usually referred to as "neglect of core polarization by the valence field" [53,54]. With approximation (51), one can compute the pseudopotential  $V_R^{(\mu)}(\epsilon, r)$  as a function of energy  $\epsilon$  by assuming a given model form for the pseudo-orbital  $\varphi_{\mu}^{\nu} \approx \widetilde{\varphi}_{\mu}^{\nu}$ , and using known HF solutions for the core  $\{\psi_{D}^{\nu}, \epsilon_{D}^{\nu}\}$ . Eq. (46) is then solved self-consistently [using the HF core integrals  $J_{\nu}$  and  $K_{\nu}$  in (50)] to obtain consistency in  $\epsilon$  between successive iterations and maximum similarity between the model  $\widetilde{\varphi}_{\mu}^{\nu}$  and the solution  $\varphi_{\mu}^{\nu}$  of (46). This defines a self-consistent potential  $V_R^{(\mu)}(r)$  in terms of the assumed  $\varphi_{\mu}^{\nu}$ , for each state  $\mu$ , to be later used to replace the core electrons in molecules and solids.

Calculations along these lines performed by Abarenkov and Bratzev [66], Abarenkov and Heine [53] and Szasz and McGinn [49] have indicated that if the pseudo-orbitals were chosen to be smooth, the resulting pseudopotential was highly oscillatory, and alternatively, if the pseudo-orbital coefficients  $\langle \tilde{\varphi}_{\mu}^{V} | \Psi_{\nu}^{C} \rangle$  were chosen to make the pseudopotential smooth, the resulting self-consistent pseudo-orbitals  $\varphi_{\mu}^{V}$ , were not smooth. This poses some problems for calculations employing real-space expansion techniques, since more basis functions would be required in LCAO. It also causes severe problems in calculations such as the nearly free electron scheme, based on reciprocal space expansion, in which the pseudopotential and pseudowavefunctions are required to have a rapidly convergent Fourier representation. This observed behavior has discouraged many workers in the field (e.g., refs. [53,54]) and has led to abandoning the first principle pseudopotential approach in favor of model potentials which are not constructed from valence functions like (48) and lead to some compromise in the smoothness of the pseudopotential and pseudowavefunctions [54]. We note that no such problems occur with the first principle pseudopotentials described in sections 2 and 3 of the present paper. Neither the pseudo-orbitals nor the pseudopotentials oscillate [16,28], because of the smooth, nodeless character of  $\Phi_{nl}^{g}$  in (6).

The self-consistency cycle encountered in the solution of (46) in the PK approach converges to a solution of the form (48). Since, however, both  $\psi_{\mu}^{v}$  and  $\psi_v^c$  are degenerate solutions to (46) with the same energy  $\epsilon$ , any arbitrary linear combination of core components (e.g., arbitrary  $a_{un}$ ) can be mixed into the solution, and still yield a valid energy eigenvalue, but might introduce oscillations in  $\varphi^{v}_{\mu}$  (even if the trial  $\widetilde{\varphi}^{\rm v}_{\mu}$  did not have them) that are apparent also in  $V^{(\mu)}_R(r)$ . In contrast, the HF and LDF pseudopotential schemes described in the present paper proceed by fixing the energy  $\epsilon$ , to coincide with the  $\mu$ th valence eigenvalue and determine the  $a_{\mu\nu}$  coefficients to produce the desired features in  $\varphi_{\mu}^{v}$ . They do not contain arbitrary core components. This also implies that although the PK scheme guarantees the correct eigenvalue  $\epsilon$ , it does not assure any meaningful wavefunction, unless  $\widetilde{\varphi}_{\mu}^{v}$  is carefully chosen to prevent convergence to an undesired result.

One can compare the PK scheme to the angular projector schemes used here, by considering the system for which (51) holds, i.e., a bare core. The HF effective potential is given by

$$V_{(r)}^{g,eff} = U_{nl}^{g}(r) + \langle V_{nl}^{g,tot}(r) \rangle, \qquad (52)$$

which, for a bare core, yields

$$V_{(r)}^{\text{g,eff}} = U_{nl}^{\text{g}}(r) - Z/r + \sum_{n'l'}^{\text{c}} 2J_{n'l'}^{\text{g,c}} - K_{n'l'}^{\text{g,c}},$$

which can be compared with the PK form (46)

$$V^{\text{g,eff}} = V_R(\epsilon, r) - Z/r + \sum_{\upsilon}^{c} 2J_{\upsilon}^{\text{g,c}} - K_{\upsilon}^{\text{g,c}}.$$
 (53)

Hence, for the bare core, the present pseudopotential is formally analogous to the PK pseudopotential: compare  $U_{nl}^{g}(r)$  in (16) with  $V_{R}$  in (47) with the coefficients  $(\varphi_{\mu}^{v}|\psi_{\nu}^{c})$  replaced by  $C_{nl,nl'}$ . However, for most systems of interest containing more than one valence electron, (51) does not hold in the HF scheme, and one has to use the generalized Phillips-Kleinman potential [11]:

$$V_R^{\rm GPK} = -HP - PH + PHP + \epsilon P , \qquad (54)$$

where P are core projectors, in place of (47). In this form, the pseudopotential becomes rather difficult to employ since a complicated mixture of core, valence and pseudo-orbitals enters the expression for  $V_P^{GPK}$ .

In the LDF approach, the total potential is state independent; hence, both core and valence orbitals are eigenstates of the same hamiltonian and the original Phillips-Kleinman form (46) holds. The effective potential in the PK form

$$V^{\mu,\text{eff}} = W^{\mu}_{\text{tot}}[\rho(r)] + V^{(\mu)}_{R}(\epsilon, r) , \qquad (55)$$

should then be compared with the angular projected LDF effective potential (generated from state  $\mu$ )

$$\{W_{\text{tot}}^{\mu}[\rho(r)] + U_{nl}^{\mu}(r) - W_{nl}^{\mu,\nu}[n(r)]\} + W^{e,\nu}[n(r)].$$
(56)

Hence, for the reference state both forms are analogous, while for a general state  $e (\neq \mu)$  one has in principle to recompute the potential (55) from the *all-electron* (valence + core) density, while in the form (56) the potential in the curly brackets is fixed at the reference state and the valence  $W^{e,v}[n(r)]$  is computed from the *pseudo* charge density. There is hence an enormous simplification in the angular projected LDF form (56) relative to the PK form (55). Note that in many calculations using the PK form, the all-electron density in the state of interest is approximated by the pseudocharge density, and their difference ("orthogonality hole") neglected [12,13] or approximated by some form [27].

### 7. Summary remarks

We have attempted to derive from a rigorous firstprinciples approach angular-momentum-projector pseudopotentials for use within the HF and LDF schemes for calculating atomic wavefunctions. While several marked similarities exist between the two, we also feel that there are significant differences. In general, the most important differences (cut-off of the potential for  $l \ge l_{core} + 1$ , relation to frozen core, energy dependence) tend to favor the LDF procedure, since both pseudopotential and LDF procedures attempt to deal with a smoothed wavefunction (LDF by a gradient expansion in the density, pseudopotential by removing from the valence functions the wiggles required for core orthogonality). Numerical tests for a number of atoms and states indicate that the LDF pseudopotential procedure is fast and accurate, at least for the first row. We have also compared our first-principles pseudopotentials with semi-empirical pseudopotentials and with Phillips--Kleinman forms, and feel that, for LDF calculations, our potentials are less arbitrary and should be of greater utility.

Of course, the real value of such pseudopotentials lies in applications to electronic structure studies for atoms and molecules. Because of the nature of most working LDF codes, only for plane-wave expansions (see section 5.4) is our pseudopotential easy to implement. Nevertheless, we feel that it possesses great potential for providing an avenue toward accurate, valence-only LDF calculations.

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