



Contemporary pseudopotentials—Simple reliability criteria

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require that the normalized pseudo-orbitals χ_n span the space characteristics of the all-electron density function. It is that of Harris and Jones (for Si) in which the orbital energies as well as the wavefunctions of a density-functional atom were fitted within a postulated local form $V_{\text{loc}}(r)$. A good fit has been achieved within a hard-core (strongly repulsive

(9)

at small- r) form. A similar approach has been successfully applied by Louie to a Pd surface.¹⁶ As this approach is completely non-empirical, the one-to-one correlation effects can be

assessed. Recent tests on the Si_2 molecule² and bulk Si⁴ indicate

that the total valence energy of the system is in good agreement with the all-electron results. This is due to the fact that the unitary mixing. In addition, one can

of the calculation the true valence orbitals

orthogonalization

in an ansatz $\chi_n(r)$ as there

control that dictates its shape at small r . No

empirical data are used. The form of

to fit some theoretical constructs of an all-electron calculation on a reference system. A recent example of a model potential problem

problem

$$\chi_n(r) = \sum_{n'} C_{n'n} \chi_{n'}(r)$$

$$n(\mathbf{r}) = \sum_{nl} \chi_{nl}(\mathbf{r}) \chi_{nl}(\mathbf{r})$$

where the sum extends on all (known) core and valence

orbitals of symmetry

is unchanged by

recover at the

simply by core

E. First principles pseudopotentials

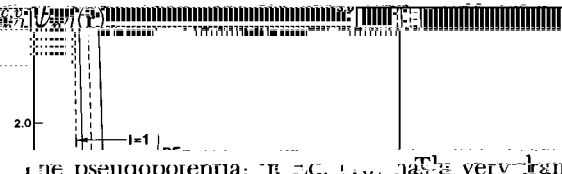
electronic configuration (g) of the atom and *sovereigns* Eqs. (8)

and $\chi_n(r)$ for the potential $V_{\text{loc}}(r)$ that is a series of these in a range

is a simple

empirical data

$$U_l(r) = \frac{1}{n_l} \sum_{n'} C_{n,n'}^{(l)} \psi_{n'l}(r) \quad (11)$$

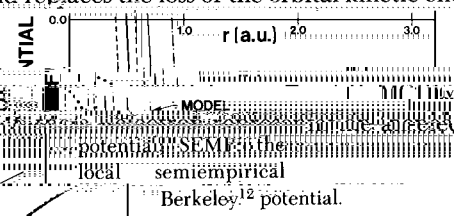


potential $U_l(r)$ contains all physical interpretation of the

states with matching symmetries in the core (e.g., Si 3s,3p), $U_l(r)$ is strongly repulsive (with a small- r behavior of C_l/r^2)

FIG. 1. Si pseudopotential and replaces the loss of the orbital kinetic en

elimination of the nodal character in χ_{nl} . For valence states with no matching symmetries in the core (e.g., carbon 2p



kinetic energy cancellation is, partial cancellation of $\nabla^2 U_l$ by the core attraction $-Z_n/r$ is taking place.

potential seen by the core electrons in the atom. The term

3. Difficulties with the DF and TDF pseudopotentials

forms a good first order approximation to the crystalline

The DF and TDF pseudopotentials are sensitive and nearly localized states in molecules and surfaces carry many of the characteristics of the atoms. The following problems:

extent that the atomic and ionic pseudo-wavefunctions mimic the atomic and ionic wavefunctions. As a result, the DF and TDF pseudopotentials are not suitable for a wide range of ground and excited states (i.e. configurations).

TABLE I. Comparison of the absorbed energies ϵ and ϵ_d and the total energy difference ΔE (in eV) as obtained by the full all-electron (AE), the pseudopotential (TDF), the nonlocal plane density functional (DF), the one-mode local potential of Jarris and Jones (MODEL), the local semiempirical Berkeley (SEMP), the nonlocal density functional (DF) and the one-mode local potential of Jarris and Jones (MODEL).

ϵ_{3s}	ϵ_{3p}	ϵ_{3d}	ΔE_1		
					$3s^2 3p^2$
AE	0.000	0.000	0.0		
TDF	-9.782 [0.01]		-3.209 [0.003]		0.0
DF	-9.782 [0.01]		-3.209 [0.003]		0.0
MODEL	-9.585 [0.019]		-3.238 [0.03]		0.0
SEMP	-10.000 [0.031]		-3.289 [0.08]		0.0
$3s^1 3p^3$					
AE	-10.522		-3.764		6.664
TDF	-10.525 [0.003]		-3.766 [0.002]		6.669 [-0.005]
6.645 [0.02]					
DF			-10.480 [-0.04]	-3.730 [-0.03]	
6.437 [0.23]					
MODEL			-10.305 [-0.22]	-3.782 [0.02]	
7.257 [-0.59]					
SEMP			-11.307 [0.79]	-3.912 [0.15]	
$3s^1 3p^2 3d^{0.5}$					
AE	-6.255		9.188		9.188
TDF	-6.255 [0.00]		9.188 [-0.004]		9.188 [-0.004]
DF	-6.255 [0.00]		9.188 [0.03]		9.188 [0.03]
MODEL	-6.255 [0.00]		9.188 [0.03]		9.188 [0.03]
SEMP	-6.255 [0.00]		9.188 [0.03]		9.188 [0.03]
$3s^1 3p$					
AE	-3.249	14.038			-18.571
TDF	-3.250 [0.001]	14.041 [-0.003]			-18.562 [-0.01]
DF	-3.250 [0.001]	14.041 [-0.003]			-18.562 [-0.01]
MODEL	-3.250 [0.001]	14.041 [-0.003]			-18.562 [-0.01]
SEMP	-3.250 [0.001]	14.041 [-0.003]			-18.562 [-0.01]
$3s^1 3p^2$					
AE	-27.932	-20.032	-10.320	29.589	
TDF	-27.932 [-0.06]	-20.032 [-0.05]	-10.320 [0.02]	29.589 [0.02]	
DF	-27.932 [-0.06]	-20.032 [-0.05]	-10.320 [0.02]	29.589 [0.02]	
MODEL	-27.932 [-0.06]	-20.032 [-0.05]	-10.320 [0.02]	29.589 [0.02]	
SEMP	-27.932 [-0.06]	-20.032 [-0.05]	-10.320 [0.02]	29.589 [0.02]	

some are affected only because the absolute energies within ± 1 eV are essentially carried over to the solid and the Si₂ molecule. In

electron moments. Numbers in brackets indicate percent error relative to

TABLE II. Comparison of the *s* and *p* pseudo-orbital moments with the

$\langle r^2 \rangle_s$ (a.u.)	$\langle r^2 \rangle_p$ (a.u.)	$\langle r^2 \rangle_{3s}$ (a.u.)	$\langle r^2 \rangle_{3p}$ (a.u.)	$\langle r^2 \rangle_{3d}$ (a.u.)
10.083	3s ² 3p ²	2.178	2.877	5.555
10.081 [0.02%]	AE	2.180 [-0.1%]	2.887 [-0.35%]	5.553 [0.04%]
5.337 [3.9%]	TDF	2.180 [-0.1%]	2.887 [-0.35%]	5.553 [0.04%]
5.337 [3.9%]	DF	2.180 [-0.1%]	2.887 [-0.35%]	5.553 [0.04%]
5.337 [3.9%]	MODEL	2.180 [-0.1%]	2.887 [-0.35%]	5.553 [0.04%]
5.337 [3.9%]	SEMP	2.180 [-0.1%]	2.887 [-0.35%]	5.553 [0.04%]
2.144	3s ² 3p ³	5.369	9.268	2.840 [1.1%]
2.157 [0.6%]	AE	5.373 [0.07%]	9.278 [0.1%]	2.840 [1.1%]
2.157 [0.6%]	TDF	5.373 [0.07%]	9.278 [0.1%]	2.840 [1.1%]
2.157 [0.6%]	DF	5.373 [0.07%]	9.278 [0.1%]	2.840 [1.1%]
2.157 [0.6%]	MODEL	5.373 [0.07%]	9.278 [0.1%]	2.840 [1.1%]
2.157 [0.6%]	SEMP	5.373 [0.07%]	9.278 [0.1%]	2.840 [1.1%]
2.073 [-3.3%]		5.137 [-4.3%]	8.968 [-3.2%]	2.993 [5.8%]
2.270 [+5.9%]		5.858 [+9.1%]	9.887 [+6.7%]	2.993 [5.8%]
2.320 [+4.0%]		5.858 [+9.1%]	9.887 [+6.7%]	2.993 [5.8%]

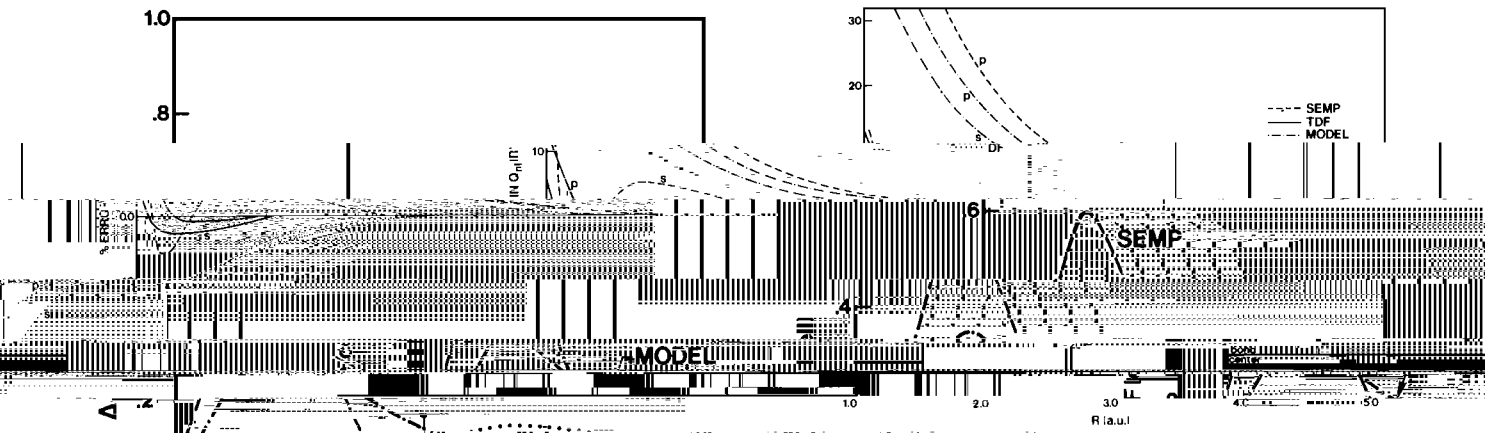


Fig. 5. Percent error in the orbital charge accumulation functions of Si. The vertical bars indicate the position of the Brillouin center in the Brillouin solid.

all-electron case.

It is seen that the SEMP and MODEL pseudopotentials produce values for L_{eff} that are considerably too large (in

Fig. 6. The errors in the pseudopotential x-ray scattering factor, relative to the all-electron result. The vertical bars indicate the magnitude of the excess value of the pseudopotential (Coulomb and exchange) interaction.

Fig. 6. The errors in the pseudopotential x-ray scattering factor, relative to the all-electron result. The vertical bars indicate the magnitude of the excess value of the pseudopotential (Coulomb and exchange) interaction. In the first few reciprocal lattice vectors, the errors in the core attraction terms of potentials, introduced by the penetration of charge into the core (and reflected by overly attractive Coulomb and exchange interactions) are particularly large. The errors in the core attraction terms of potentials, introduced by the penetration of charge into the core (and reflected by overly attractive Coulomb and exchange interactions) are particularly large. The errors in the core attraction terms of potentials, introduced by the penetration of charge into the core (and reflected by overly attractive Coulomb and exchange interactions) are particularly large.

the self-consistent calculation with $U_{\text{eff}}(r)$ are then described by the inhomogeneous Schrödinger equation $H_{\text{eff}}\psi = E\psi$ for the sort semempirical local SI pseudopotentials (see also Ref. [10]).

constitutes an enormous simplification over the direct solution of the all-electron problem, such a core orthogonalization (performed *after* the completion of the solution of the pseu-

TABLE IV. First principals density-functional results for the band gaps of some cubic materials compared with experimental data.

the para-structure mode. It is a common mistake to assume that the simplicity of the para-structure mode is a simple consequence of the simplicity of the para-structure mode. It would seem that one of the more important challenges of the contemporary many-body theory is to construct (seemingly) one-body potentials that would yield consistently better results.

¹³M. J. Appelbaum and D. R. Hamann, Phys. Rev. B **8**, 1577 (1973).

¹⁴Reporting the pseudopotential single-particle Eq. (2) in the form: