PH YSICAL REVIE% B VOLUME 18, NUMBER 10 15 NOVEMBER, 1978 First-principles

18 F IR S T-P R IN CIP L ES N 0 N LOCA L -PSEUD D 0 POTE N T IAI.

only a small number of parameters V„,(C,),
where 0,. is a reciprocal-lattice vector. System-
atic extension of this approach is possible via the
introduction of additional parametric forms in V„„
describing the energy and angular momentum de-
pendence of the pseudopotential" (nonlocal correc-tions). As the separation of the potential indicated in E[l. (5) is not done in the EPM, this approach is not limited by the frozen-core approximation and attempts to mimic core polarization and relaxation effects. The SSPM approach"

"
treats the valence

field by a microscopically defined theory [e.g., Hartree-Fock" (HF) or local-density functional (LDF)"], but parametrizes a chosen model form for V» to ionic term values" or to the band struc-
ture.

"

Since in this approach V„, depends on the
actual solutions X, through the screening valence field V„(K,X']), self-consistency in the description is possible in principe. e. In the NEMP ap-proach,

""

V„ is again treated rigorously while
V» is fitted to theoretically calculated all-electron atomic eigenvalues.
In contrast to all the model potential approaches,
the first-principles pseudopotential approach re-
tains the rigorous relation (3) and attempts to cal-culate both V» and V„ from a microscopic theory without restricting them to any model functional form. Both the successes and the failures of this theory in reproducing the observed data can in principle be analyzed in terms of the underlying microscopic interactions in the Hamiltonian (e.g., electron correlation}, subject to the pseudopoten-tial frozen-core approximation. Further, property
(3) enables the retention of the desirable features in the pseudo-wave-functions (such as expandability
in simple and convenient basis functions, similar-
ity to '

good" all-electron wave functions, etc.)
and recovery, to within a good approximation, of the true wave functions, simply by core orthogon-aliz ation.

First-principles pseudopotentials have been pre-
viously obtained with the HF scheme by several workers,

'"'"'"

and were used for molecular

structure studies. Recently, Zunger et al.
have suggested a method for obtaining first-prin-
ciples pseudopotentials in the local-density form-
alism which e are

form-

interactions

andctual approximation,

the

underlying8Tj ET B4 /Xi6 9..95Tf 147.47 9 642.18 Td (and)Tj5ET B46/X92 9.. s

microscopic1.89 ET B4 /Xi2 9.12 Tf 939.76 2 227.41 Td (and)Tj ET B3/Xi12 7.53 Tf 1129.62 Td (First-principles)T36ET B352/42 7.539Tf 129.88 4y.83 Td (studies.)ET B32

5452 ALEX ZUNGER AND MARVIN L. COHEN 18

correlation potentials are, respectively,

V„(n,(x))=

~

[

dr', n,(r')

5Z„,(,(~))

5n, (r)

and the density n, (r) is.related self-consistently to the eigenvectors of Eq. (8}by

~,(~)

= Q&:g

~

x'.
(

(&)

~ '

(10)

Here ¹,denotes the valence occupation number

in the ground reference state g, and the sum is ex-tended to include N„electrons. 'The inhomogeneous exchange and correlation potential V„,(n,(r)) is normally replaced by the homogeneous free-elec-
tron potential V„,(n (r)) in the usual way, '

leading
to an exchange part V„(n,(r)) [with exchange coef-ficient a = g' (Ref. 42)] and a correlation part V,(n,(~)) for which we adopt the results of Singwi et al.'~ Gradient corrections '~'

are possible,
but will not concern us here. Note that as the den-

sity n, (x) would be constructed to be slowly vary-ing over space, the neglect of the higher terms in the gradient expansion is more justified than in the all-electron LDF approach.
One now seeks the form of the external potential V,„,(r) such that for the reference electronic state g, the eigenvalues of Eq. (8) will equal those of the all-elecj, ron problem:
[--s'&'

—(Z„+Z,)/r+ V„(Pg(x)) + V„,(p, (r))]g'„,(r)

= e'„,g'„,(r), (11)

and that the

FIR ST-P R I N CIP I, KS NON I. 0C A I, -PS K U 0 0PO T E N

5454

10

(aj

UNGEg AND MAAR@IN L. Cp HEN

(b)

&S

0

0
0
0

18

5

ST PRINQIIPLES NONLOLOCAL -PS KU D

I I (

LO - OPOTENTIA L

4 =0

Core: 1s, 2s, 2p I 3sI 3p
I

I

I
I I

I

(a)

Mo
Tc
Ru
Rh

—10
5

(b)

0

0

—10—

(b)

Q -5
C
I
0
Q
—10
10

Mo
Tc

Rh,

Ru

4=2 (c)

—10—

—10— —20—

—15— —30—

—20
0 1.0 2.0

R (a.u.)

3.0 4.0

FIG. 3. Core potentials o

'

of the first, 3d

E-l .() —

' '"'"'"""

—40 I
0 1.0 4.0

I I I I I

2.0 3.0

R (a.u.)

FIG. 4. Core potentials of
(b) t= d(c l=2.

si ion series (a)

lim U, (x) (21) = C,/2

for l+ L where t
h

ls a os

f

U, (x) re 1

n. It is

e po n 1als in

i

1 p

th th an core states

l.e.,
es as the lowest

solutions) tha
that in

n the a
th

all-electron

a'o h e
a cance liat

but rather corn

cine-Abarenkov'4

Z0 j
ov '

potentials)

1milarity const
ation in E~

ance, given up the req
s — unction match

a the

egree possible f

ill t ti i

i i
th here the

e

pseudo- orbital

ALEX ZIj NGER AND MARVIN L. COHEN 18

0.5—

I

(a)

= 0

Li

0

I

c 05—
0
CL

)

(b)

—0.5—

—1.0

0).0 2.0
R (a.u.)

3.0 4.0

FIG. 5. Core potentials of the alkali atoms. (a) l = 0, (b) l=1.

g„,(r) is identified in Eq. (12) with a 1s orbital [having no nodes but lacking similarity to the val-
ence state)(„,(r)]. This lea.ds to U, (r) = c„,—e„,
exactly like the Phillips-Kleinman form, ' with lit-
tle pseudopotentia. l cancellation. Clearly, this re-sulting core potential would yield the correct val-
ence eigenvalues in Eq. (2) (simply by shifting the
1s level by an amount necessary to make it degen-erate with the valence orbital of interest), but would lead to very poor valence wane functions

The highly repulsive character of U, (r), l & f, for
small r and the associated degree of pseudopoten-
tial cancellation is hence a natural consequence of
the maximum similarity constraint on the pseudo-
wave-functions, which assures in turn its vari-
ational quality. Note that the repulsive nonlocal
potential U, (r) is short range under the maximum similarity constra;int; if R, denotes a dista, nce from the origin at which all core orbitals have al-ready decayed to zero, it is clear from Eq. (15) that for r&R, one gets U, (r)=0. Hence, although determining the behavior of the pseudo-wave-func-tions in their tail region, U, (r) is confined to the core region. We note that both the empirical and the semiempirical core potentials used for solid-state applications usua, lly lack this

FIRST-PRINCIPLES NON LOCAL-PSKUDOPOTEÃTIAL...

zero as Z„/r [e.g., Fig. 3(c)]. For I present in the core, they start out as C,/r' in the inner core, have an l-dependent classical turning point 0 [W,(6) = 0] and a negative minimum WP"= W, (rP")
at y', ", and then approach zero as -Z„/r [e.g.,
Figs. 3(a), 3 (b) and 4]. Their essential new feature relative to many of the empirical model potentials

is the occurrence of the turning points '

r',. These
are strongly nonlocal and characterize the prop-erties of the atomic core in that they represent the point where the repulsive Pauli potential, mod-ified by orthogonality hole effects, equals the at-tractive electron-nuclear

tnd

5458 ALEX ZUNGER AND MARUIN L'. COHEN I8

states of l = 0 and l =1 symmetry approaches unity
and U, (x) becomes

18 FIRST-PRINCIPLES NON LOCAL-PSEUDOPOTENTIAL...

the values and regularities in some relevant oper-
ator expectation values obtained with the "true"
all-electron orbitals. We know that the expectation
values of the Hamiltonian operator are, by con-
struction, exactly reproduced for the reference
ground state of the atoms. Other operators that might sample the pieces of the wave functions which are relevant to bond formation in condensed

systems are x ', r, 2, &', etc. In particular, the various moments of x are useful in depicting the

detailed deviations of g from (in the various re-
gions of space, as in a direct comparative plot they are hardly visually distinguishable in the tail regions.
Figures 8-12 show the trends in the moments of
r for both the all-electron (full circles) and the
pseudo- (open circles) wave-functions for atoms of rows 1-5. Both sets of wave functions were ob-tained from a self-consistent numerical integration of Eqs. (11) and (8), respectively, with an accur-
acy

ALEX ZUNGER AÃD MARVIN L. COHEN

20— (a)

24—

20—

0
12—

v 8

0 I
2.6

2.4—

2.2

2.0—

1.8—

, 1.6—

1.4—

0

I I I I I
I I I

0

16—
0

CV

12—

8—

p I
4.0

3*5

3.0—
0

2.5—

2.0—

b
b

FIG 9 Orbital moments
for the valence electrons
of the second-row atoms.
Full and open circles de-
note all-electron and
pseudopotential results,
respectively. (a) 3s, (b)
3p. The Bd orbital mo-
ments are identical by
definition,

0.8—
I

D

0 0

0.4—

&r ')„

1.5
1.0

0.8—

0.6—
0

~r o ~or
~8

0.2— 0.2

0 I I I
Na Mg Al

I I I I I

Si P S Cl Ar

p
Na

I I I I I I I

Mg Al Si P S Cl Ar

I I

4.0— gO0

3.6—

0
3.2
L

2.8—

'8~

.p~ /o ~~r

24—I I I I I I I I I I I
I I I I I I I I I I I

0.50—
~ I

I

0.40— r~O
L O~

/ ~O p

.O---O ~O rOr

~

Or

0.30 or
Ca Sc Ti

I I I I I I I I I

V Cr hhn Fe Co Ni Cu Zn Ga

FIG. 10. Orbital moments for the 4s states in the first-
row transition atoms. Full and open circles denote all-
electron and pseudopotential results, respectively.

appropriate symmetry, the order of improved can-
cellation remains l = 0~ l = 1 ~ l = 2. Clearly, the consta, ncy of the orbital kinetic energy ratios with-in rows reflects the fact that the pseudopotential
transformation we used retains the regularities of
the orbital localization present in the all-electron
picture. In contra. st, there is no guarantee that the wave-function systematics would be preserved in either the model potential approach""

"
or the

Phillips-Kleinman" approach. Unless special care is taken, these wave function need not reflect the
characteristic features of the true orbitals. '.
Still a different measure of the quality of the
pseudo-wave-functions is provided by the calcu-
lated x-ray scattering factors F(Q) We find th.at
the deviations of the pseudopotentia. l atomic sca,t-
tering factors from the corresponding quantity computed with the true valence orbitals does not exceed 2%, and is very small relative to the num-ber of valence electrons. Some typical examples are given in Fig. 14(a), where the core charge density was simply added to the valence pseudo-
charge-density in calculating F(Q). The errors
are seen to be located almost equally at low and

18 FIRST-PRINCIPLES NONLOCAL-PSEUDOPOTENTIAL... 5461

18—

16—

14—
0

5462ALEXZUNGERANDMARVINL.COHEN18
0.45
0.40—
0.35—
Q
0.30
0
IIIIIIIII—o—AEx0.1
--0--PS
50
E
0
U
30
C
0
I
20
a)
0.25I
C
(V
I0.20
C
0
0.15
0
0.10—
0
0.05—
0IIIIIIIII
NbMoTcRuRhPdAgCdIn
FIG.13,Comparisonofthe5sorbitalkineticenergy
perelectronofthefourth-rowatomsobtainedintheall-electron{0)andpseudopotential(0)calculation.The
all-electronresultsaremultipliedbyafactorof0.1.
10
0
0.2—
E
0
0
0.1—
—0.1—
Q
U
—0.

of

FIGaj
ET
BT
/Xi13 7.9 T6f
249.21 923.70 Td
(I)T
0.

FIRST-PRINCIPLES NONLOCAL-PSEUDOPOTKNTIAL

tal core potential W„,(r)

ALEX ZUNGKR AND MARVIN L. COHEN 18

band widths of the solid. Clearly, if one wants to study different energy regions in the condensed phase (e.g.

, outer-core states or highly excited
Rydberg states), one would have to construct

a

new potential based on

a different electronic

FIRST PRI NCIPLES NONLOCAL-L-PSEUDOPOTENTIAL... 5465

in the moments over d

the pseudo- wave- f

t'

a wi e energy ran e. ge; while
ve- unctions are

5466 ALEX ZUNGER AND MARVIN L. COHEN 18

iently low energy bonding (or

FIRST-PRINCIPLES WONLOCAL-PSKUDOPOTKNTIAL...

FIRST-PRINCIPLES NON LOCAL-PSKUDOPOTENTIAL... 5469

TABLE V. Energy eigenvalues and orbital

ALEX ZUNGKR A WD MARV JN L.