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Self-consistent yseudoyotential calculation of the bulk yroyerties of Mo and W
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(transition-metal compounds and surfaces) with
reasonable accuracy.
The calculation of the pseudopotential total ener-
gy can be greatly facilitated by the use of the mo-
mentum- space r epresentation r ecently developed. '
This avoids any muffin-tin approximation to the charge density and replaces the complicated six-dimensional integrals characteristic of first-prin-
ciples real-space representations '

by simple and
readily convergent reciprocal-space lattice sums.
The mixed-basis representation of the crystalline
wave functions""' similarly permits an accurate description of both the localized and the itinerant
features of d-band transition metals. The density-
functional exchange3 and correlation" functionals are used to self-consistently describe the valence screening in the system. As the core pseudopo=
tentials are similarly derived from the density-
functional one-body equations,

'

this approach is
completely nonempirical and enables a direct as-
sessment of the quality of the presently known
local-density exchange and correlation functionals for the description of ground-state proper ties of
transition metals.

(2)

The all-electron charge density p{r) is given by the
core + valence wave functions gq(k, r) as

p(r) = Q N;(k) ~ gf (k, r) g~(k, r) ~, (3)

gyA

whereas the pseudo-charge-density n(r) is simi-
larly constructed from the Fermi-Dirac occupation
numbers Nz(k) and the pseudo-wave-functions
Xz(k, r} as

n(R =+ Ng(k) ~XP(k, r)xq(k, r) ~

. (4)

While o{r) contains contributions from N, +N„core and valence electrons, n(r) is normalized to N„. The valence potential V"(n(r}j has the same func-tional form as the total core+ valence potential, except that it acts on the valence subspace only.

II. PSEUDOPOTENTIAL TOTAL ENERGY
I

The pseudopotential formalism' replaces the
all-electron (core+valence} eigenvalue problem

[-&V + Vt,',"g(r)jjgz(k, r) =e&(k}g&(k,r), (1)

where g&(k, r) and e&(k) are the jth-band wave func-tion and energy eigenvalue, respectively, and

V;,'",g(r)jis the total potential (containing elec-
tron-nucleus, Coulomb electron-electron, and exchange and correlation terms due to all the elec-trons), by a simpler equation pertaining to the sub-space of the valence electrons only

[-a& + V"{n(r)j+V (r)])(~(k, r)=e~(k)y~(k, r).

More specifically, in the density-functional ap-proach, 3

it is given as

V"(n(r)j= g =+ I ———,dr' n(r')

Ir-R I ~ tr- r'I

m

+ V„(n(r)j+ V„„„fn(r)j.

Here Z„ is the screened nuclear charge of the atom at the lattice point R„and V„(n(r)j, V „(n(r)j, and V„(r) are, respectively, the local exchange and correlation potentials" and the pseudopotential. In general, V„(r) is a nonloeal potential construct-
ed as a lattice sum of the individual single-site
pseudopotentials U,(r} of angular momentum I, as

V„(r,r') = P U, (r —R„,r'-.R)P~P',

m l=0

A(where P& '

is the angular-momentum projection
operator with respect to site m.
To the extent that the construction of U&(r) can be
made sufficiently simple, the effective one-body equation (2) is significantly easier to handle than
the all-electron equation (1) in that a smaller num-
ber of electrons (N„rather than N, +N„} has to be
treated and the wave functions)(&(k, r) can be made spatially smooth (due to the absence of the core orthogonality constraint) and hence are expandable effectively by convenient basis sets. Whereas U,(r) has been traditionally treated as an empiri-cally parametrized quantity adjusted to fit either the low-energy interband transitions e&(k}—ez,(k), 9 Fermi surface and resistivity of metals or the ionic term values, ' we have derived U&(r} for all atoms of rows 1-5 in the Periodic Table by a di-rect inversion of all-electron Eq. (1) in the atomic limit. The construction of the single-site pseudo-

m705.74 T4n

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nr V r+V„„r r
Z2

+E„,{n(r}]++(

mAn m

and does not depend explicitly on the pseudopoten-
tial. Expressing the total exchange and correla-
tion energy E„,{n(r))by its approximate density-functional form'

E (r(r)}—=„fn(r)r„(rr(r)}dr, (8

where e„,{n(r)]=e„{n(r}]-+e,{n(r)j is the exchange and correlation energy per particle, which is re-lated to the corresponding one-body potentials by

V„{n(r)}=-',.„{n(r)),

V „{n(r)]=e,{n(r))+n(r) de, {n(r}]
one obtains the expression for E„,expressed by
direct-space quantities as

Et, (. ——Q N)(k)e~(k) ——,dr dr' 1 n(r)n(r')
1 (I n(r) V„(r)dr
4

+ n(r)[e {n(r)]

Zv —V,.„{n(r)]]dr+Q-

mgn m n

(10)

The first term is the sum of the one-body eigen-values over the occupied portion of the Brillouin
zone (BZ}, while the second term is the correction
due to the overcounting of the interelectronic Coul-
(

tional throughout. This should enable a direct mea-
sure to the quality of the presently known many-
body correlation functional in predicting ground-state properties of solids. We extend this study presently to the calculation of the total energy and bulk properties of solids.
The total energy associated with the variational equation (2) is given by

omb repulsion. The third and fourth terms are corrections to the exchange and correlation ener-gies, respectively, while the last term is the core-core nuclear repulsion term. The corresponding equation pertaining to all the all-electron case [Eq. (1}]is formally identical with Eq (1.0}when the pseudo charge density n(r) is replaced by the all-electron density p(r) and the valence charge Z„ is replaced by the atomic number Z.
In practice it appears to be difficult to obtain E~, for a solid directly from Eq. (10) for the gen-eral case where n(r) [or p(r)] is unrestricted to

re- form'

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V.(r) = VL(r) + Vmz, (r)

~«t

Rm~ ~g

UL,(r-R„-re)

Here Vc,„& denotes the electron-electron repulsion
term [second term in Eq. (5)], n

)Z+) is the 6 =0
component of the repulsive local pseudopotential
of atom P, and Es„,q~ is the Ewald core-core en-ergy. 3 The primed sums indicate omission of the G =0 term from Vc,„,(G) and G ",„denote the sum-mation limit. The local pseudopotential is defined by arbitrarily partitioning V~(r) into a term acting

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Flo. 1. First-principles nonlocal core
f o1 bd

e ine: l =1; dashed-dotted line: l = 2.

[i.e., i=1, I =22, and -2 ~ m (2 in Eq. (15b)] and
n y& such that the basis function
~

q~rg match the initial rise of t

in Eq. 18

or atomic Pseudoorbitals. We th en use G~2'„

q. () as a convergence parameter
ing it until all ener

arne er, increas-
n i a energy eigenvalues containin d ch
aeter stabilize to with' 0 01. ns
approximate linear d

in. eV. It turnsns out that
e xnear dependence (monitored by the

trix" d

smallness of the eigenvalues of th e overlap ma-} does not occur within this choice u t

in e energy eigenvalues requires ~G' '

G&3& 12

=15 Ry (or about 110-140 plane p ane wwaves' and
=55 Ry (or 730 plane waves. Fo

'

cu a ion usin g a pure plane-waves basis
i.e., a,„-=0in Eq. (15b}]a corn p ar

cut

s plane waves in the bas Th
off values are required b th

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ly localized nature f th d

e o due to the relati

and the needed hi h r

e o e potential U'
e sg precision in e&(k) for a total

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I.O —'

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0 0.4 0.8 1.2 0 0.4 0.8 I.2 l.6 0

D I STA N CE (UNITS OF a)

I I I I

0.4 0,8 %

FIG. 2.

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field Vc,„,+ V„+V„„in these equations [derived
from the variational charge density through Eqs.
(20) and (22)] is in fact identical to that used in the
one-body Eq. (2). If the potential V„used in Eq.
(2) (V„=Vc',s„, + V„"a) is different from that derived
from the variational density (Vg,"„,+ V„""), the. second and third terms in (11)read

E,.„,+Z„= gn(G)[-,'Vc',"„,(G}-Vc",„,

ALEX ZUNGER AND MARVIN L. COHEN]9

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atomic sites

atomic

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TABLE III.

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TABLE IV. Components of the total energy of tungsten and molybdenum at the calculated equilibrium lattice con-stant. 20 k points are used to sample the BZ. E',"t de-notes the spin-polarized atomic total pseudopotential energy. All quantities are given in Ry.

Quantity

QiV)(k) a')(k)

n(G) V„,{G)
G

2 Q &(G)Vcocl(G)

—Qn{G)Vx(G)

AZy

@Ewald

gn(G) a,(G)

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J. (19722 ET BT /Xi14 8.89 Tf 35.29 32242 346D. 47 569(48)TjDET BT /Xi14 8.61 Tf 95.96f 1559(47Xi14 8.64 TfTd (Ged.73 Td ((b))Tj ET BT /Xi14 12 69.27 4C8 Tf 235.81 372.48 ema)Tj ET BT /Xi14 7.58238.42 9f 2Tj ET

v.

K,

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andTdTj ET 4BT / ET 1f 86.83 Tukey 516.529Td (J.)Tj5, BTi14 7. .99 Tf 115Mat 1559(47Xi14 8.64)Tj ET B4591714 7.46.6 Com 8.14 Tf 399.8 Td (287)Tj E

Bev. O.4 55 385.'ET9Tj ET384 8.4 Tf 236.52 Tf u ET68.77 55 385.'ET9T ET 41T /Xi Tf .07 7f1 0.61 T443.3.515.87 |OAg

A Td ('3R.)T18ET B 4

507Tj 6 BT /T /XiBT 247Tf 155. 1 Tf 172.5336Tj07Tj 6 BT /T BT /Xi14 8.5 Tf 19326 336.36 Td07TjET BT /BradlT / ET 1f 86.83 Tuk925 529.4461

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