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Calculation of the electronic properties of Mo in a first-principles nonlocal-pseudopotentiai approach

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582 ALEX ZUNGER, G. P. KERKER, AND MARVIN L. COHEN 20

and energies) good agreement (-10

s Hartrees) with
all-electron results is found over

a large range of ex-
citation energies. We have recently applied these pseu-
dopotentials to study phase stabilities of binary solids' and to electronic properties of semiconductors.

"

In contrast to the semiempirical pseudopotential ap-
proach, 6' the first-principles pseudopotential method
does not assume any ansatz form for VI(r). In turn, its shape both in the core and the valence regions is automatically determined (numerically) by the max-imum similarity and minimum kinetic energy con-straints. We find that these potentials are strongly repulsive in the core regions, quantitatively reflecting the effects of the replacement of the radial nodes in the all-electron wave functions by nodeless, smooth maximum-similarity pseudo wave functions. We find in fact that this repulsiveness, as reflected in the oc-currence of zero-energy turning points rI of

20 CALCULATION OF THE ELECTRONIC PROPERTIES OF Mo IN... 583

10

—10—

—15—

—20
0 2

r (a.u.)

primarily to produce a fast convergence in momen-tum space, e.g., Refs. 6, 7) might introduce an
unwarranted energy dependence, '

its form-
unrestricted generation directly from the variational

eigenvalue problem' "yields a nearly energy in-
dependent and accurate potential.
The pseudopotentials sho~n in Fig. 1 are much deeper and more localized than those pertaining to

nontransition elements. ' The depth of the I =0, 1,
and 2 potentials is —5.80, —5.77, and —35.54 Ry, respectively, and the classical turning points occur at 0.84, 0.89, and 0.20 a.u., respectively. Clearly, the
conventional plane-wave representation of the crys-
talline wave functions is largely ineffective for such systems. %'e next discuss the mixed-basis representa-
tion' for the electronic states.

S. Eigenvalue problem

584 ALEX ZUNGER, G. P. KERKER, AND MARVIN L. COHEN 20

where R„and v denote the direct primitive lattice
vector and the sublattice coordinate, respectively, and
N is a normalization constant. The basis orbitals

20 CALCULATION OF THE ELECTRONIC PROPERTIES OF Mo IN...

s-d contribution. Figure 2 shows a contour plot of
the corresponding momentum representation of
F~(Q, Q') for I = I and 2. It is seen that these contri-
butions peak at about Q

= Q' =7.35 a.u. '

for the s-p
n ET BTKlocalityT BT /Xi4 8.22 Tf 70.221 65 (=1 Td1(s-p)T(withT BT /Xi4 8.34 Tf 244.913954.06 Td (Q')TjET BT /Xi4 8.83 Tf4943.53 764.87 Td1(s-p)Tsei-)d

t636534= n ET j ET BT /Xi4 8.76 Tf0183.385154.063656(=7.)TwhilET BT /Xi4 8.55 Tf 177.45 5f 24636534= '=1 7109Q' 'n ET higheET BT /Xi4 8.54 Tf7343.53 7122 1f0183mentum 2THE =3.53 Td (.5 71 (plot)whilET BT /Xi4 8.55 Tf 177.4584d 9m5 71 4for)Tj ET BT /Xi4 8.1 Tf 271.630665.25 719s-d =

586 ALEX ZUNGER, G. P. KERKER, AND MARVIN L. COHEN 20

TABLE II. Self-consistent wave vector and band-de endent w

'

p 's

jp[XJ(kpr lxll kp, r)~, where X(k, r) is the s
sum o weights is normalized to unity.

kz point band 1 band 2 band 3 band 4

1 1 1

(—8'&' ———)

8

(0,—,

', 0)

1 1 1

(—8'8'8——)
1 1 1

(—4'4' ———)

4
1 3 1

(—8'8' ———)

8

(——0) 1 1
(0,—,, 0)
1 3 1

(—8'8'8——)
1 1 1

(—4'4'4——)
3 3 3

(—8'8' ———)

8
1 1 1

(—4'4' ———)

4
3 3 1

8'8' 8
(—2'2',—, ——)

2

(0, 0, 0)

0.020 833 3
0.020 833 3
0.031 250 0
0.020 833 3
0,041 666 0
0.052 083 3
0.015 625 0
0,036458 3
0.010416 66
0.010416 66
0.036 458 00
. 0.026 041 60
0.005 208 33
0.005 208 33

0.020 833 30
0.020 833 30
0.031 250 00
0.020 833 30
0.041 666 00
0.052 083 30
0.015 625 00
0.036 458 30
0.010416 66
0.010416 66
0.036 458 00
0.026 041 60
0.005 208 33
0.005 208 33

0.020 833 00
0.019904 60
0.031 250 00
0.020 032 40
0.039 931 80
0.050 367 50
0.012 880 40
0.034 51986
0.010416 66
0.006 446 70
0.030 672 55
0.022 071 70
0.002 03930
0.005 208 33

0.005 692 60
0.003 13820
0.003 555 30
0.003 15920
0.003 565 40
0.003 334 40
0.0
0.0
0.0
0.000 242 20
0.001 021 80
0.000 51440
0.0
0.002 634 66

the wave-function expansion.
A compatible convergence in the Fourier r tation of

20 CALCULATION OF THE ELECTRONIC PROPERTIES OF Mo IN...

Table III we have collected the energy eigenvalues at
some high-symmetry points, relative to the calculated
Fermi energy. The same table contains

ALEX ZUNGER, G. P. KERKER, AND MARVIN L. COHEN 20

—8

of the BZ and then transferred on

a grid of 512
points throughout the whole zone by making use of the point group symmetries of the crystal. The Fourier coefficients of the energy bands

Ctl)

I

X (k)

—k Yl
K

(14)

were obtained using

a fast Fourier transformation.

N is the number of grid points. The number of grid points

R was then increased by

a factor of 64 to

a

mesh of 32 768 points. Interpolated values for e„(k) are found by an inverse Fourier transformation on the large mesh setting C&R =0 on the additional points. The rms error of this interpolation scheme is less than 0.

1 eV for all bands except at crossing
points ~here the error can be of the order of 0.

2 eV.

In Table IV we compare for

a

k point which does not
belong to the original 35 points the results of the fit with the energy bands calculated directly by solving the eigenvalue problem. The agreement is within less than 0.

1 eV. The density of states is given by

D(e)

=

—Xg(e

—e„(k)) N-

k, n

(15)

For the histogram in Fig. 4, we used an energy chan-nel width of 0.1 eV. The Fermi energy eF is found from the integrated density of states

N(.

)

=

J D(.') d.', (16)
using the criterion N(eF)

= Z„, where Z„ is the
number of (valence) electrons per atom (Z„=6 in the case of molybdenum).
The calculated density of states is shown in Fig. 4.
Three main structures are observed below the Fermi energy and two peaks with

2 eV above E~. These are
compared in Table

V with the available photoemis-

sion data. ' The peaks at —3.96, —2.92, and —1.67
eV are very close to the high-symmetry points N'2 (d~ -type), P4 (d~+ +~-type),

20 CALCULATION OF THE ELECTRONIC PROPERTIES OF Mo IN...

of V, Nb, and Ta, it has been suggested that the two
prominent low-energy peaks at 2.35 and 4.1 eV arise

from g, X, and G~ G~ transitions, respectively,
while the wide absorption in the 11.5—20-eV region
arises from transitions to unspecified empty d states.
Using a minimum slope difference criteria between initial and final states, we find that the peak along

X, should occur at 2.'55 eV at about —,

590 ALEX ZUNGER, G. P. KERKER, AND MARVIN L. COHEN 20

4L

E

sf

E
sr

FIG. 7. Band charge density in Mo at the N point in the
(110) plane. Full dots indicate atomic positions. Values are given in elcell, normalized to unity; (a) N& (band 3), (b)
N) (band 4).

FIG. 6.

4nd

20 CALCULATION OF THE ELECTRONIC PROPERTIES OF Mo IN... 591

N H

FIG. 8. Total valence pseudopotential charge density of
Mo in the (110) plane.
N

D. Fermi surface

Detailed theoretical and experimental studies of the Mo Fermi surface (FS) have been given by several
authors. A relatively complete survey is presented in
Ref. 27. We have used the results of our Fourier fit to obtain information about the Fermi-surface di-

mensions of Mo within the first-principles pseudopo-
tential method in Fig. 9. We have plotted the cross section of the Fermi surface in the (100) and (110) planes in analogy to Ref. 27. Bands 3 —5 contribute to the FS. Contribution of band 3 is purely hole-like and consists of an ellipsoid around N and an oc-
tahedron around H. Band 4 is an electronlike jack

around I, finally band 5 contributes a small electronlike lens centered along the b-symmetry line which is nearly circular. In Table VI we compare the FS cross-section dimensions along high-symmetry directions with the calculations of Koelling et al.
obtained from a relativistic APW (RAPW) calcula-

FIG. 9. Calculated cross sections of the Fermi surface in the (100) and (110) planes of Mo.

tion, the results of Boiko et aI. 47 obtained from the radio-frequency size effect (RFSE) and the results of Cleveland et al. 48 obtained from the de Haas —van Alphen (dHvA) effect. Considering the relatively small amount of primary points included in the Fourier fit the agreement is quite remarkable. We do not get, of course, a jack-octahedron separation be-
cause our calculation is nonrelativistic.

IV. CONCLUSIONS

The first-principles nonlocal pseudopotential
method is shown to provide an accurate representa-tion of the bulk electronic properties of molybdenum. . Within this approach, the band structure, the density

0

TABLE VI. Fermi-surface cross-section dimension in A

'

for Mo.

Direction This
Work

Ref. 27
RAPW

Ref. 47
RFSE

Ref, 48
dHvA

Band 3 (hole)
Octahedron [10o]
[110]

0.80
0.66

0.81
0.60

0;79
0.60

0.81
0.61

N ellipsoid Nr
NH
NP

0.35
0.25
a95 Tf 28lm 66RAPW

ALEX ZUNGER, G. P. KERKER, AND MARVIN L. COHEN

of states, charge density, and the Fermi surface can be reproduced in reasonable agreement with other calculations and experiment. Together with a mixed-basis representation of the crystal wave func-tion which accounts for both the delocalized nature

of the s and p electrons and the strong localization of the d electrons, this nonempirical self-consistent pseudopotential approach provides a very efficient

technique for electronic-structure calculations.

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20 CALCULATION OF THE ELECTRONIC PROPERTIES OF Mo IN... 593

~5D.