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atomic sites o,' of the same chemical type o. with symme-try operations (e.g.,

the diamondlike structure), we can
l—0

defin vsLDA(r) vLDA (r). The subs«rpt "SLDA'
denotes "spherically approximated LDA." Thus we will
make the following spherical approximation of Eq. (5):

Vr.DA(r) ~ Vsr, nA(r) =)„). vsL'DA(lr R, I). (7)
We de6ne as C the reciprocal lattice vectors of struc-

ture o with unit cell volume 0 and as V(C) the Fourier
transform of V(r). The nth atomic structure factor of
structure a is

0]. In both cases the nonspherical error is assessed by

calculating b, Vi of Eq. (9), and is called the error of
"strictly forbidden reBections. "
There is another kind of error. The solved

vsfL'DA(IG I)'s are a set of numbers corresponding to a
discrete IG I

set. The plot of vs„nA(IG I) vs IG I

can

involve some scatter, so the individual points cannot be
described by a single smooth curve (which is needed in
our search for a r-space continuous pseudopotential). We refer to this as scatter error. We examine its conse-

quences by fitting the points (vsfL'DAl(IG I), IG I) for a
given structure o to a parametrized form

3. S(~,~l (G) 0))

R

where g~ stands for summation over R 's within

r

one unit cell. In this notation, the spherical approxi-
mation of Eq. (7) implies the neglect of the following
nonspherical potentials:

20
2 2

SLDA (g)) SLDA ()

(G)

= "Sr.'DA(IG I) —usL'nA(IG I) (12)

Then, the "one structure scatter error" for structure o is
calculated as

+Vi (~) LDA(~) SLDA(~)

LDA(G-) —Q S' "'(G-) vSLDA(IG-I).
(9)

vr.nA(G) =) s

'

(G) vsL'DA(IG I) (10)

This quantity [AVi]

is called the error of "strictly for-
bidden reBection" due to reasons explained later.

To solve for vsfL'DA(IG I), we will first solve Eqs. (1)—
(3) within the LDA (using ab initio nonlocal pseudopo-tentials) for a set of structures and unit cell volumes denoted collectively by (o'), finding the self-consistent

Fourier coeKcients VLDA(C) of Eq. (5). We then at tempt the equality

where v denotes the (numerical) solutions to Eq. (10) and u denotes the fitted value of Eq (ll). The error AV2 reflects the neglect of the scatter of vsLDA(IG I) for a single structure, which is another manifestation of the error in the spherical approximation. Combining the "strictly forbidden reflection" error EVr of Eq. (9) with
the "one structure scatter error" AVz of Eq. (12), gives
the total error due to the spherical approximation for a given structure o.

2. The str uetuv al aces age aper oximation

So far, the potentials vsI, DA and us&'D& depend on the crystal structure o. We now average over a number of

difFerent structures (o). Thus, at the right hand side of
Eq. (7), we perform the replacement

for each structure o. We solve Eq (10) for each G

which has a nonvanished VLDA(G)

and flnd real val-

ued vsfL'DAl(IG I). The spherical approximation of Eq.
(7) maiiifests itself by the fact that the solution of Eq.
(10) is not always exact (or even possible), thus the er-

ror AVi (C)

in Eq. (9) is nonzero. Equation (10) can
be considered as a matrix linear equation for each G
with o. and real and imaginary parts as its column and
row indices, respectively. Because, this matrix could be
singular, the solution could be not exact ~or even pos-
sible). A simple example is when Sf l

(G) = 0 but
VLDA(C) g 0. These are called "forbidden reflections, "
e.g., G = ((222), (442), (622), (644), and (842)) for the
diamond lattice, G = ((004), (014),(031), and (033))
for wurtzite, and G = ((002), (004), (024), and (114),

004),2 Td ((024),)Tj ET59 1054 Td ((Tj ET BT /Xi2 9T BT /Xi2 9d2Tj ET Tf 270.88m.33 104.BT /Xi2 8.6n5T BT /Xi2 9(due)Tj 2.44 124.733 Td EX)Tj ET BT /XiF

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3 (~) SLDA(l ~l) SLDA(l&-I)

Note that this "structure averaged scatter error" LV3
difFers &om the "one structure scatter error" AV2 [Eq.
(12)] in that the former involves structural averages in
the Gtting of u. Consequently, the magnitude of the error
4V3 is larger than the magnitude of 4V2.

.

the increase

reBects the error introduced by structural average.
At this stage we have a spherically symmetric and
structural averaged, screened atomic LDA potential
us&D&, this will be called the SLDA in the following dis-
cussions. We will examine the errors LVj, LV~, and
AV3 defined in Eqs. (9), (12), and (15), respectively. In addition, to test the eKect of the total error LVi+LVq collectively we will solve the band structure of Eq. (4) [replacing v&)(~r —R ~) by usfLDA([r —R [)] and com-pare the resulting eigenvalues e,, wave functions g,, and related properties with those obtained by solving self-consistently the original LDA Eqs. (1)—(3) for the same
structures.

We close this section by noting that if one wishes
to perform non-self-consistent (e.g., Harris-functional-

like)

electronic structure calculations, usLDA(r) can be
used as an excellent input potential.

B. Using the SLDA to construct the semiempirical
pseudopotential method (SEPM)

Our next task is to adjust the SLDA potential of Eq.
(14) so that the ensuing wave functions of Eq. (4) will still retain a high overlap with the LDA wave functions of Eqs. (1)—(3), yet the eigenvalues will fit the experimental (or quasiparticle calculated) excitations. In this process, the ab initio nonlocal potential V„„i,i(r) of Eqs. (2) and (4) (which represents the effects of core electrons) is kept unchanged as in the reference LDA calculations. Furthermore, we use the same analytical form of Eq. (14) for both usfL)DA(q) and usfE)pM(q): the coefficients will

change from CsLDA(n) to CsEPM(n) while b and c will be kept fixed.
The Gt to the observed excitations is chosen

can

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TABLE III. The "one structure scatter error" AV2 [Eq. (12)] for particular CdSe structures and cell volumes per atom n, and the "structure averaged scatter error" Evs [Eq. (15)] involving the variance with respect to the structurally averaged potential. Here, Op is the equilibrium wurtzite CdSe cell volume per atom and Qp is the equilibrium diamondlike Si cell volume per atom. The numbers in the

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tures is as small as & 70 meV. This suggest a good struc-
tural transferability of us&&A (q).
To examine this point we compare the band structures

obtained using in Eq. (4) us&&&(q) with the band struc-
ture obtained in direct LDA calculations. This compari-
son is given in Tables IV for CdSe in the wurtzite struc-ture, in Table V for CdSe in the rocksalt structure, and in Table VI for CdSe in the zinc blende structure and a deformed wurtzite structure. The root mean square (rms) differences between LDA and SLDA band ener-gies are about 50 meV, consistent with the overall error

in us&&'A (q) discussed above. To see the effects of hy- (cv,se)
drostatic pressure we give in Tables IV and V the en-
ergy difference e'(Ao) —e(Bi) for two unit cell volumes (Op and Oi) as computed in the LDA and SLDA meth-ods. This comparison shows that the average error in hydrostatic deformation potential of SLDA relative to that of LDA is about 20% for wurtzite CdSe and 8%%uo for
rocksalt CdSe. Besides the five CdSe structures men-
tioned above, we give in Table VI the band energies of
wurtzite CdSe but with randomly displaced atoms (of
the order of 4% of the bond length). The band energy
difFerence e,(B; + b) —e;(R;) between this deformed
structure (B; + 8) and the original wurtzite structure
b = 0 reQects phonon deformation potentials. The aver-age phonon deformation potential difI'erence between the LDA and SLDA is about 20%.

For Si systems, instead of showing all the band edge states as we did for CdSe, we give in Table VII only the rms and maximum band energy difFerences between the SLDA and LDA. Here, we include most high symmetry points for each structure (e.g., L, I', A, and K for the di-amond structure) and all eigenstates up to 4 eV above the conduction band minimum for semiconductors and

4 eV above the Fermi energy for metals. The average

SLDA vs LDA energy difFerence is about 60 meV, similar

to the potential error of us&&z(q). Notably, the energy

(s)

errors for simple cubic, simple hexagonal, and P-tin struc-
tures are much smaller (

15 meV) than those for the
diamond structure. This is consistent with the fact that

the potential errors (Table III) of the former structures are smaller than those in the diamond structure. The hydrostatic deformation potential difI'erence between the SLDA and LDA is about 18% for the diamond structure. Table VII gives the energies of the diamond structure with randomly displaced Si atoms (by 10% of the bond length). The error in the phonon deformation potential
is about 14%. Table VII also shows predictions for ad-
ditional crystal structures, not used in our fits. These
include the fourfold coordinated BC8 structure, which has eight Si atoms per unit cell and an atomic volume of 0.9100'. The average SLDA vs LDA band energy error is 75 meV, only slightly larger than the errors for the struc-
tures included in the Gt. We also tested the simple face
centered cubic structure, which is a 12-fold coordinated system with an atomic volume of 0.7200'. The average SLDA x s LDA energy error is also 75 meV.
To summarize the energy errors we can say that the spherical and structurally averaged potential us(&&A(q) reproduces the original self-consistent LDA band ener-gies to within 0.1 eV or better for a range of difFerent crystal structures, including those not used in its con-struction.

We next discuss the accuracy of us&&A(q) in reproduc-ing LDA tvave functions and related properties. To this end, we have calculated the overlap between the SLDA
wave functions g; IEq. (4)] and the LDA wave functions
g; [Eqs. (1)—(3)j. The results for CdSe in the wurtzite
structure and for Si in the

Si

functiohe BT /Xi6 8.45 Tf 152 349.222.44 Td ((functions)Tj ET BT /Xi6 11 T3.78 370 10.0 Td (the)Tg;)Tj ET BT /Xi6 9.81 Tf862.22 4007.44 Td (energy)T BT /Xi6 8.8 Tf 5

th0 /Xi6 9.66SEPM.9 Tf 528.22 689.22 c t5Xi6 818 /Xi6 9.44 Tf 325.11 574.33486.78 Td (at2i6 9.2 Tf j ET 7 9. Tf 398 584.67 Td (i8f5280 ((of)2i6 T /Xi6 BoT /X9t1/Xi6 9.09 n57ducto2 2(of)2i6 ET BT /Xi6 9.34 Tf 314. Felated7jT BT/Xi6

.4810ETLDA

.487ET BT /Xi8.22 434 Td (or)T

phononond

for

1BT /Xi6 9.6f 398 584.67 Td /Xi6d en(o7ET Bs ET BT9 (LDA)Tj .22 434 Td (or)Tj 65j ET i8T BT9 (.08 Tf 5897 Tf 314.44 542.5jj ET2 ET BT8 (LDA)Tj 4.22 434 Td (or)T222ble)2926 Tf ETLD 1BTXi6 98+G 398 584.67 Td /Xi6tructu

phon3 701.lotd (for2y)Tj ET BT85.78 616.33 Td (is)T4Tj E3(up)Tj1BTXi6 933
LDA

LDA

or(B35ti15 17 (LDA)Tj 842 434 Td (better)TT Td (i4 (ET 16 (LDA)Tj 8.22 434 Td (or)T33Tj ETT BT /X16 (LDA)Tj 176)Tj ET 1217381.d (5 BT Tf 2sn)T159

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TABLE IX. Momentum matrix elements M;&
)(g;~p~gf)(for wurtzite'CdSe and for diamondlike Si as
obtained by various approximations. Here, LDA, SLDA,
and SEPM denote, respectively, the LDA [Eqs. (1)—(3)],
the LDA with spherically symmetrized local potential, and
the empirically adjusted SLDA. The unit for M, &

is bohr

The notations "6.

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LDA S
33
20
wurtzite
6.40
7.16

SLDA
6.8+G
5.6+G

E,„t, for CdSe (Ry)
E,„t, for Si (Ry)
e,(J)
6.34
7.07

CdSe

M's = (ilplf)
M'f = (tip+ ',„If)—
M'f = (ilp+ g'g(&+ G)lf)
M,s = (alp+ ~„(v+G+ w)l f)

6.52 4.66 4.85
7.30
7.48
7.63

5.19
5.31
5.40

TABLE X. The static dielectric constants e, of CdSe and Si as calculated using Eqs. (17) and
(18) and different sources for the transition matrix element M~f between initial (i) and final (f) electronic states. p denotes the momentum operator, while V, G, and W are the nonlocal potential, the 8 nonlocal Gaussian correction, and the smooth E,„& operation, respectively, as discussed in Ref. 31. k denotes a wave vector in the bulk Brillouin zone. LDA, SLDA, and SEPM denote, respectively, the LDA IEqs. (1)—(3)], the LDA with spherically symmetrized local potential, and the empirically adjusted SLDA. EPM stands for the Bergstresser-Cohen empirical pseudopotential for CdSe (Ref. 34) and the Chelikowsky-Cohen nonlocal empirical pseudopotential for Si (Ref. 35). The correct matrix element form is M,f = (ilBH/Bkl f) when compared to the experiment. J and II denote perpendicular and parallel to the c axis of the wurtzite structure, respectively.
LDA SEPM EPM
33 6.8+G 33
20 5.6+G 20

CdSe wurtzite e, (ll)
6.43 6.32
7.15 7.01

M*t = ('lplf)
M'y = (' Is + g, If)
M;f ——('lp+ s'A,.(&+ G)lf)
M;f ——('Ip+ —, '„(&+G+ ~)If)

6.64
7.33
7.50
7.61

4.88
5.37
5.49
5.57

4.68

M'x = (ilplf)
M'f = (&I&+ 'gg If)

(tip+

G)lf)

Si

and

6.

49

6.

4.09when 88

4. 88

6+G 32

6+G 88

6+G 66

5.

61

85 5.

5.

48

5. 33(&I&+

66 u t S axis
in5. b nonlocal empirical adjusted

4

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tional EPM wave functions.
In Table IX, we have listed the matrix elements
I(g;Iplgf)l of the SEPM results and the traditional
EPM results for CdSe wurtzite structure and Si dia-
mond structure. The matrix elements of the SEPM fol-
low closely the LDA and SLDA results. On the other hand, the matrix elements of the traditional EPM m. -y sometimes dier from LDA results by a factor of 2. (c) SEPM optical properties. The SEPM density of
states and the dielectric constants e2(E) are shown in
Figs. 9(a)—9(c) for CdSe and Figs. 10(a) and 10(b)

for Si. The density of states compares very well with the experimental data, ' especially the peak positions. For CdSe, however, there are a number of discrepancies caused by the neglect of the Cd 4d orbits in our pseu-dopotential treatment. (i) The width of the CdSe upper valence band in Fig. 9(a) is smaller than the experimen-tal value. This is partly caused by our neglect of the Cd 4d states. Because of p-d coupling, the 4d state will push up the top of the valence band resulting in an increased upper valence band width. (ii) The optical absorption spectrum eg(E) of CdSe agrees very well with the exper-

TABLE XI. Comparison for CdSe of band energies (in eV), band gap Eg (in eV), and effective
masses (in units of electron mass) as obtained in the LDA, the LDA with spheri44 546Td 44 546.11 Td (LDA,582t1.78 546.11 Td

s (the8.54 Tf.5 12 .26Xi12a12 8.211 Td (s (t596.22 Td (CdSe)Tj153314Tj ET BT /Xi12 9.5 Tf) 332.453314Tj T /Xi1f 473.89 670.33 Td (orbits)Tj ET BT //XidSe Td (band)Tj ET BT / e.26lemlnts

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and SEPM), the ensuing wave functions have & 99.9%
overlaps with the original LDA wave function, the rea-
son for this must be rather general, and not a unique
property of the GTV correction. The reason might be
that the original LDA band energies are close enough to
the experimental results so that small Hamiltonian mod-
ifications LH are enough to correct them by first order
perturbation Ae; = (@;~AH~g;) without changing the
wave functions.

The change from SLDA to SEPM [us@pM —us&D&] (Figs. 4 and 5), although always small, is dependent on
the detailed choices of the weights m; and u in Eq.
(16). This nonuniqueness is a manifestation of the em-pirical nature of the fitting. A more ab initio approach, using the SLDA and some approximated form of GW
self-energy, might overcome this problem.
Our semiempirical pseudopotential is designed for bulk
systems. It can be applied to the most common struc-
tures that exist for that material. It can be applied to
different volumes for each structure and to the phononic mode of that structure. It remains to be seen whether

it can be used in alloy systems, where the type of neigh-boring atoms for a given atom can change. It could be
that some environment dependent scheme, like the lin-
ear interpolation method used in Mader and Zunger's

appoach, " is necessary. The current potential cannot
be used in cases where large charge transfer exists, so
probably it cannot be used for surfaces.
In summary, we presented an approach to generate
semiempirical pseudopotentials. Comparing to the tra-
ditional EPM approach, the current method has the fol-lowing features. (i) A spherically and structurally aver-aged screened LDA potential, SLDA, is generated. This
potential can be used to reproduce the LDA band en-

ergies (within 0.1 eV) and wave functions (with overlap) 99.99%) for the most common bulk structures of that

material. (ii) The SEPM is fitted from the SLDA. Be-
cause the change is very small, many physical trends of
the SEPM follow the results of the SLDA (thus LDA)
without explicit fitting. FTd (t28l74.89 TBT /Xi15 9.42 Tf 197.11 329.22 Td (the)Tj ET BT /Xi15 9.26 Tf 224.67 429.22 Td (thansfer)abiliy)Tj ET BT

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sutting.Tj ET BT /Xi15 8.1 Tf 134.67 397 Td (n&m)Tj ET BT /Xi15 9.54 Tf 533.56 617 Td (nL

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the band structure (in the long quantum well calculation
mentioned above, the erroneous lowest eigenstate disap-
pears). One minor inconvenience af this approach exists:
when a constant potential Vo is added to the original po-

tential V of 0, using this cutoK method, the resulting H'
is not simply subjected to a constant shift in energy. In our calculation we fix the original potential V by requir-ing the vacuum level to be zero. Another smooth cutofF method which avoids this inconvenience is to change H to 2(G —k) iv (G) + Vic(Gi, G2)

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Estimated from the difference between experimental e2(E) and the SEPM e2(E) at E 14 eV, the contribution of 4d electrons to e, is on the order of 0.

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R Td (E.)Tj ET BTBT /Xi18 10.2 Tf 161.33 451 42 Td (6.

CoeMoscTj ET BT /Xi18 8.94 Tf 343.7 431.738,

Nauka, NaTj ET Be ETctiv/Xi18 8.46 Tf 464 68 663.240TTj (NaTj ET B /Xi18 8.59 Tf 351.36 632.352Td (58)TTj ET Bj ET BT Xi18 8.7 Tf 445.78 622.58 Td (K.)Tj ET BTtransiBT /Xi18

and5(1967);)T /Xi18 8.35 Tf 430.56 704.332Td (Nils67);)Treasonable/Xi18 9.63 Tf 65.22 502.4Td ((19)Tj0.67 /Xi18 8.9 Tf 253.5.18673.33 Td (1319)Tj0.67 /Xi18 8.24 Tf 20

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B60Tj ET BT34/Xi18 9.26 Tf 443.5 420.65V7