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New approach for solving the density-functional

NEW APPROACH FOR SOLVING THE DENSITY-FUNCTIONAL...

Theophilou (see also Refs. 5 and 6) has shown that for any physical charge density n (r) there ex-ists a potential U,„,(r

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with d electrons, and the structurally complex ter-
nary semiconductor CuInSe2.

II. FOUR VIEWS ON THE TOTAL-ENERGY-
MINIMIZATION PROBLEM

A. The wave-function sampling method

and Sham have provided a particular interpreta-tion to it, based on a wave-function variational principle BE„,/BQ=O. This leads to the condition for the gradient:

BEtot

Ba,j Ba,j

2

~ + VKS[«r)]

In this approach one must (i) select a trial parameter set Ia;~] for Eq. (5) and construct the wave functions fz(r; Ia;~ I

) of Eq. (5); (ii) construct
the density n(r) and kinetic energy T[n] from Eqs. {3}and (4), respectively, and (iii) calculate E„,[n, V,„,] of Eq. (1) and repeat the above steps to obtain the minimum of E«,[nta&];V,„,] as a function of I a,J.I.
The primary advantage of this method is that it does not require any eigenvalue problem solving, such as Eq. (2), and does not require that any ef-fective potential be constructed. Hence, it is possi-ble to deal conveniently with nonlinear parameters and interelectronic correlation effects directly in the wave functions. Consequently, this method has been used extensively to calculate many-body in-teraction energies for bosons, nuclear matter, Fer-

mi liquids, solids, '

and molecules" with the use
of nonlinear forms such as the Jastrow wave func-

tions' QI(r iz, t a,z J

) or Feenberg wave functions

Pj(r, 2,r, 2s,..., I a,j I

). It has also been used to
define Wannier functions for solids. ' However, for our purpose here of treating systems with a large number of occupied single-particle orbitals

tgj], this method is very ineffective because it re-quires a good search method to converge at all and since the number of its variational parameters de-pends on the number of occupied orbitals. It is therefore limited, with the use of state-of-the-art nonstochastic search algorithms, to about 100

parameters a,j. The result is that this method is
suitable for independent-particle problems only
when the number of occupied states is small (as simultaneous minimization is required for all single-particle orbitals g~) or when the wave func-tions have a particularly simple form. Many prob-lems in contemporary one-electron solid-state phys-ics do not satisfy thee conditions.

B. The wave-function gradient,
or the HKS method

Since the form of the energy-minimizing poten-tial U,„,(r) of Eq. (2) is generally unknown, Kohn

(7a)

to be satisfied by the final SCF wave functions g*(r). This is more commonly identified as the Kohn-Sham (KS) single-particle equation for the variational wave functions of the fictitious nonin-

so 543.56 TdTd (Tf 4 Tf T /0a 8.75 (numbTf 3154 176.79 Td lesradient:)Tj ET BT /Xi2 1333 Tf .71 67 153.[adient:)Tj ET BT /6Xi2 9.16 Tf 4.65 153.—adient: r,

form t

the

66.17 443.19 188.44di51 Td (nary)Tj ET BT /Xi2 8420 61i443.521 422.5 Td (fTd ({3})Tj ET BT /Xi2 10.57./Xi147.83 560.81 Td (of)Tj ET BT /4T /Xi2 3.31 .05 85 211.(However,)Tj ET potential r,nu +„,

(iii) form

T[n]

numb.2 Td (')Tj ET B3 /Xi2 9.34 Tf 158.83 387.8 Td (of)Tj ET B10 /Xi2 8..48 f 224.15 688.B86 Td (n(r))Tj ET BT /6Xi2 9.33 T1 Tf45.9 350.—adient:

„,66.Tf 171.322 7

[n, +

BE„,

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with various computational approximations, in-

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[Eq. (6)]. In Appendix A we show that this condition results in

BE„, BU,„, =0=2Re ggraj (fj(r) ~ VKs —U,„, ~ Pq(r)} QJ'(r) Pj'(r) I (9)

where V~s

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orbitals for d electrons and a large set of plane waves to ensure adequate variational flexibility. Once localized orbitals have been included, the core states can be treated explicitly with no addi-tional difficulty. No pseudopotential approxima-tions are needed.

We will treat all real-space quantities (potentials,
wave functions, and charge densities) in a mixed
representation consisting of a multicenter (mc) term and a Fourier series (FS) term. The generic expression is

f(r)=g
a l,

gf~i~(r

m

~~)&i~(r r)—

B. Potential and basis sets

To describe a crystalline potential, a reasonable first-order approximation is to represent it as a su-perposition of atomic potentials. We use this ap-proximation only to guide our choice of a varia-tional form for the potential and our selection of basis functions. The

The unit-cell volume is denoted by Q and all basis functions are normalized over the unit cell.

The atomic solution used for the potential and basis functions is not the traditional isolated atom. We perform two modifications to make the results

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msx

nj(k, r}=nFsj(k,r)+ g g gn i J(k, r —r~)Y~ (r —P.).

a E=o m

Here I,„is treated as a convergence parameter. Most of the contribution to the second term is the spheri-
cally symmetrical core charge. In many previous orthogonalized-plane-wave (OPW) calculations (e.g., Ref. 28), only the I =0 term was included. The one-state densities nj(k, r) can then be summed with appropriate special k-point weighting factors to get the total density, which can also be written as having a Fourier-series and a multicenter contribution,

n(r)= ggcoj(k)nj(k, r)=nz„(r)+ggn i (r r—)Yi (r r—). (23)

A specific G component of the total charge density is given by

n(G)=nFs(G)+pe g(i) Y—i~(G) I

r drji(rG)n~i~(r). (24)

At this point one may introduce the frozen-core
approximation when it is desired. We interpret
freezing a core state to mean that the charge densi-
ty of that core band is approximated

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n,~(r)= d r n(r+r~)

4m.

=ye nFs(G)jo(Gr)+ n 0Q(r)
6

4~
(28)

and

1, r&r

1 C(r)= —1+cos m.

2

0, r, &r

r —r2
rmc —r1

r& &r&r,

(29)

where v~(G) are Fourier components of the atomic potentials, given by Eq. (B8).

IV. SEARCHING FOR THE ENERGY
MINIMUM

are the spherically symmetrized density around ~ and a smooth cutoff function, respectively. (We

use ri =1.0 a.u.) Different values will give dif-ferent f~, but must give the same v„,. Given this

definition of f, one can now evaluate the second

term of Eq. (26) on a regular mesh in real space
and use a fast Fourier transform to evaluate it in

6 space. Convergence can be proven with the use of progressively finer real-space meshes until no further improvement is obtained in the G com-ponents.
One additional point in our method is that the nonspherical density in the multicentered terms is included only

in

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IfJ' '

is the Jacobian matrix (}F(p,'

')/Bp
then this expression represents the first two terms
of the Taylor-series

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TABLE II. Silicon band energies in eV and x-ray scattering amplitudes for various con-vergence parameter setting. For each column, unspecified parameters are set at the standard values as given in the text. The results of a frozen-core approximation (FCA) are given for comparison.

State

2$
2p

r, „
I 2sv
I 15m
I2,
r„

X)„
X4„

X),
X4,

Standard

—132.5 —90.0 —11.95

0.0
2.50
3.29
7.59

7.88 —7.79 —2.90

0.57
9.99

385 pw/atom
51 pt/a. u.
24 stars

—132.5 —90.0 —11.96

0.0
2.48
3.26
7.58

7.69 —7.80 —2.87

0.53
9.96

l=o

—132.5 —90.0 —11.96

0.0
2.49
3.28
7.59

7.87 —7.80 —2.90

0.57
9.99

6 k points

—132.5 —90.0 —11.94

0.0
2.51
3.29
7.61

7.89 —7.79 —2.89

0.59
10.00

FCA

—11.94
0.0
2.50
3.28
7.60

7.90 —7.78 —2.90

0.59
9.98

Beam Scattering amplitudes (electrons per unit cell)

(111)
(220)
(311)
(222)
(400)
(331)
(422)
(332)
(511)

15.17
17.31
11.35
0.35
14.89
10.22
13.39
9.06
9.09

15.28
17.31
11.35
0.35
14.88
10.21
13.38
9.05
9.08

15.16
17.31
11.34
0.36
14.89
10.23
13.39
9.04
9.09

15.15
17.31
11.35
0.34
14.89
10.22
13.39
9.06
9.09

15.15
17.27
11.31
0.35
14.84
10.17
13.34
9.01
9.04

very stable for any basis larger than 115 plane
waves per atom. Even for 55 plane waves per
atom the maximum errors are about 0.1 electrons for the

(1112(2p)Tj ET j ET BT /Xi11 9.34 Tf 273.66 391735 Td7.72 —as7as55as

6.8er 590.181197.6ndard ——

96. —7. 9.969900

9rs

set ET BTT 6p1Xi-9.11 Tf 3i22.29 677.35 Td (v220))Ts ET BT12.41 9.9 Tgnifi8.n28.45 667.37 Td (T7)Tj ET T21 8.291.89 Tf 1154058 38 49846d8.77 text9j ETIT /Xi191 Tf 258. Tf 273.66 391735 Td7.77

99

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We thus conclude that the standard

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these states and leads to eigenvalue errors as large
as 1 eV. Similarly, freezing the Zn 3d drops this
level by about 4 eV and introduces errors in the
other bands typically of the order of 1 to 1.5 eV.
Thus, we conclude that core states can be frozen
without substantial damage, but not transition-metal d states (even in an insulator such as ZnS).

B. Comparisons with previous results

1.4—

tO,

EO

o 1.0-

—0.8—

~ 0.6— I

P 0.4-

40

& 0.2-
u 0.0
CO

SI

Interstitial Atom

-2.0 -1.0 0 1.0 2.0

This section is devoted to comparing our results with those of previous calculations. We will com-pare the silicon results with those of Hamann ob-tained with the use of the linear

C. Convergence in self-consistency

One of the principal features of our

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TABLE V. Structural parameters for CuInSe2 and convergence parameter settings for our
calculations.

Lattice type and constant Body centered tetragonal
a =10.93 a.u.
c=21.86 a.u.

Primitive lattice vectors r) ——{a,0,0)
r2——(O,a,0)
r3——(a /2, a /2, c /2}

Atomic positions

Special k points and

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BL 8

Tilt Due to Anion

Displacement

10-

Cu

Q In

Qse

FIG. 6.

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10- 10-

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TABI.E VI. CuInSe band energies (in eV) at the

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tours are at logarithmic intervals. Heavy

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Bpn(r)=—g roJ.2 Re[/~(r

)Ops (r)]

(A

j j'Qj

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where Jis the Coulomb operator 1/

~

r —r

'

~

. This equation generally is not useful for evaluating J~ ' be-

cause it requires having all the eigenfunction QJ (r), and the double sum over double matrix elements is an N process that usually is too expensive to be useful. However, the formula can be used as a guide for ap-
proximating J' ', as we do for the quasi-Newtonian method.

APPENDIX B: MATRIX ELEMENTS IN THE MIXED BASIS REPRESENTATION

The following formulas are used for computing overlap and Hamiltonian matrix elements:

&~'o ~@r, & —&oo

i Yim(k+6)e "4n I r dr ji(r

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charge. The density n(r) of Eq. (810) is used to
construct a V„,(r) by the methods of Sec. III D.
One now makes a Taylor-series expansion to in-
clude the nonspherical terms as

ing the derivative

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