PHYSICAL REVIEW B VOLUME 32, NUMBER 12 15 DECEMBER 1985

Orthogonalized linear combinations of atomic orbitals.
III. Extension to *f*-electron systems

Y. P. Li,* Zong-Quan Gu, and W. Y. Ching†
Department of Physics, University of Missouri–Kansas City,
Kansas City, Missouri 64110-2499

(Received 27 June 1984; revised manuscript received 12 August 1985)

The previously developed direct-space orthogonalized linear combination of atomic orbitals method is extended to include f-electron orbitals. All the matrix elements of overlap, kinetic energy, and one-electron potential between Gaussian-type orbitals are derived. A test calculation on the band structure of γ-Ce agrees well with other calculations.

The direct-space orthogonalized linear combination of atomic orbitals (OLCAO) method is an efficient first-principles method suitable for electronic structure calculations of low-symmetry systems.[1] In this method, an all-electron basis is used for the calculation of interaction matrix elements, but the valence orbitals are orthogonalized to all the core orbitals so that the latter can be eliminated from the final secular equation. It was shown that the eigenvalues and the eigenvectors obtained from such a calculation were as accurate as when the full basis was used;[1] meanwhile the computational effort was greatly reduced. Naturally, the method will be very useful to study the electronic structures of disordered solids or crystals of low symmetry as well as systems involving heavy metal elements which contain large cores. While the method has been extensively used for the electronic structure calculations of amorphous solids[2,3] and complex crystals,[4] its application to heavy metals involving f electrons has not been realized. Since nearly half of the elements in the periodic table have f electrons, it is desirable to extend the method to include f electrons in the calculation. Generally speaking, occupied f-electron orbitals in an atom are very localized, and a tight-binding type of approach is quite natural for such systems. Furthermore, the ability of the LCAO method to resolve the wave functions into various orbital components certainly facilitates the interpretation of many phenomena unique to f-electron systems.

We have further developed the OLCAO method to include the f orbitals in addition to the s,p,d orbitals. Previously, f orbitals had been used in the LCAO-type of calculation only for the augmentation of the basis set to achieve greater variational flexibility of the Bloch functions,[5] and was generally limited to one f-type of orbital only. Extension to include all types of f orbitals in our version of the direct-space OLCAO method is straightforward, but requires derivation of analytical formulas involving two-center and three-center integrals. In the OLCAO method, the atomic or the atomiclike orbitals are expanded in terms of Gaussian-type orbitals (GTO). These are s type ($e^{-\alpha r^2}$, denoted by g), p types (xg, yg, and zg), d types (x^2g, y^2g, z^2g, xyg, yzg, and zxg), and f types ($xyzg$, x^2yg, x^2zg, y^2xg, y^2zg, z^2xg, z^2yg, x^3g, y^3g, and z^3g). The last ten GTO listed above are used to form the seven radial f orbitals with the corresponding angular functions listed in Table I. The one-electron potential of the solid is written as a superposition of atomiclike potential functions $V^A(r)$ centered at each site constructed according to the local density functional theory and are numerically cast into the analytic form

$$V^A(r) = -\frac{Z}{r}e^{-\alpha r^2} + \sum_i C_i e^{-\beta_i r^2} \ . \tag{1}$$

We let ϕ_A, ϕ_B be the two GTO centered at site **A** and site **B**, respectively. There are three types of integrals that need to be evaluated:

$$\langle \phi_A | -\nabla^2 | \phi_B \rangle \ , \tag{2}$$

$$\left\langle \phi_A \left| \frac{e^{-\alpha(\mathbf{r}-\mathbf{C})^2}}{|\mathbf{r}-\mathbf{C}|} \right| \phi_B \right\rangle \ , \tag{3}$$

$$\langle \phi_A | e^{-\alpha(\mathbf{r}-\mathbf{C})^2} | \phi_B \rangle \ , \tag{4}$$

where (2) is the two-center kinetic energy integral, and (3) and (4) are the three-center potential-energy integrals associated with the potential (1) centered at site **C**. The special case of $\alpha = 0$ in (4) gives overlap integrals. The extension of the method boils down to the evaluation of the above types of integrals between s-f, p-f, d-f, and f-f GTO. This can be done systematically by successive differentiation of the existing analytic formulas derived for s-d, p-d, d-d, and f-d integrals. This procedure has been discussed in some detail in Ref. 6. Considerable efforts are saved by taking advantage of appropriate symmetry relations. In the Appendix, we list the above three types of integrals derived for $xyze^{-\alpha r^2}$-type of f orbitals as illustrative examples. Once all the necessary analytic formulas are derived, the rest of the calculation follows the conventional OLCAO method.[1]

TABLE I. Angular functions of seven f orbitals.

$$Y_{xyz} = \tfrac{1}{2}\sqrt{105}\,\sin^2\Theta\,\cos\Theta\,\sin(2\phi)$$

$$Y_{z(x^2-y^2)} = \tfrac{1}{2}\sqrt{105}\,\sin^2\Theta\,\cos\Theta\,\cos(2\phi)$$

$$Y_{x(x^2-3y^2)} = \tfrac{1}{4}\sqrt{70}\,\sin^3\Theta\,\cos(3\Theta)$$

$$Y_{y(3x^2-y^2)} = \tfrac{1}{4}\sqrt{70}\,\sin^3\Theta\,\sin(3\phi)$$

$$Y_{z(2z^2-3x^2-3y^2)} = \tfrac{1}{2}\sqrt{7}\,(5\cos^3\Theta - 3\cos\Theta)$$

$$Y_{x(4z^2-x^2-y^2)} = \tfrac{1}{4}\sqrt{42}\,\sin\Theta\,(5\cos^2\Theta - 1)\cos\phi$$

$$Y_{y(4z^2-x^2-y^2)} = \tfrac{1}{4}\sqrt{42}\,\sin\Theta\,(5\cos^2\Theta - 1)\sin\phi$$

Because the f-electron wave functions are quite localized, interactions involving f orbitals beyond second- or third-nearest neighbors are usually negligible and need not be calculated.

We have tested our newly constructed computer codes by calculating the band structure of γ-Ce. Recently, there has been an upsurge of experimental and theoretical interest about the electronic structure of Ce metal, especially on the subject of α-γ phase transition[7,8] and the mechanism of hybridization of f electrons and Coulomb interactions.[9,10] Our major interest in this paper, however, is to establish the reliability of our method, which has been extended to include the f orbitals, rather than to obtain a most accurate band structure and to study its consequences. We constructed the atomiclike potentials using an overlapping atomic charge-density model with the atomic wave functions of Ce (Ref. 11) in the ground-state configuration of [Xe] $6s^2 4f^2 5d^0$. The atomiclike basis functions are obtained by the method of single-Gaussian contraction from the atomiclike potential. The number of GTO used in the contraction are 13 for s- and p-wave functions and 10 and 9 for d- and f-wave functions. The use of the same set of GTO (with exponentials ranging from 0.12 to 74 000) for all types of wave functions has greatly reduced the computational complexity. The noncore portion of the basis in our calculation consists of $6s$, $7s$, $5d$, $4f$, and $6p$ contracted atomiclike orbitals. After orthogonalization to the core, the size of the secular equation to be solved is only 17×17. The calculated band structure of Ce along the symmetry lines of the Brillouin zone of the fcc lattice is presented in Fig. 1 and the corresponding density of states in Fig. 2. These bands are in good agreement with those of Pickett, Freeman, and Koelling[7] using the relativistic self-consistent augmented-plane-wave (APW) method. This indicates that the extension of the OLCAO method to f-electron systems is successful. Using Mulliken's scheme of population analysis,[12] we obtained distribution of the four valence electrons in Ce as 0.63 in the $6s$ state, 1.84 in the $5d$ state, 1.05 in the $4f$ state, and 0.49 in the $6p$ state, which indicates that substantial orbital hybridization is reflected in our calculation. The small difference between our result and that of Ref. 6 may be attributed to relativistic effects which we have neglected. A semirelativistic test calculation indicated that the relativistic effect on the band structure is quite small. With further development, refinement, and application, we expect the OLCAO method to become fully competitive with other ex-

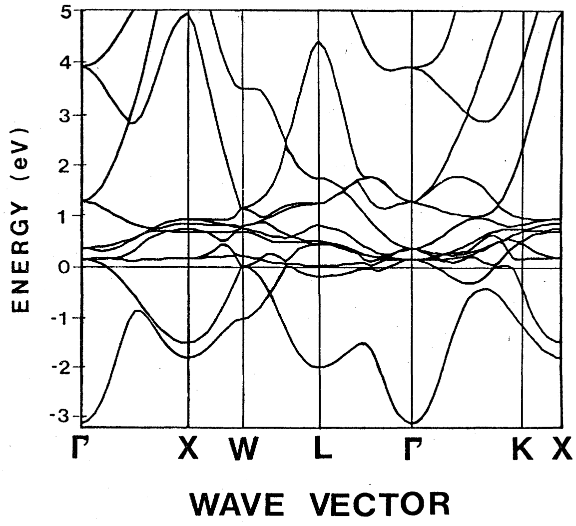

FIG. 1. Band structures of γ-Ce.

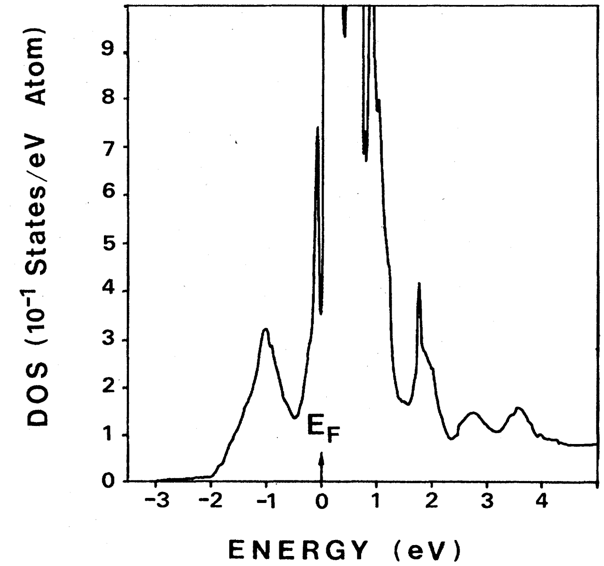

FIG. 2. Density of states of γ-Ce.

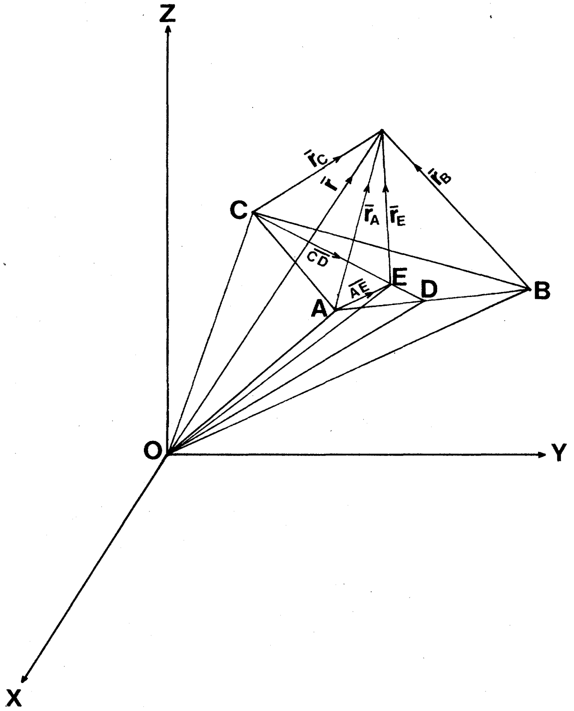

FIG. 3. Vector relationship for the reduction of multicenter integrals.

isting first-principles methods for the electronic structure calculation for f-electron systems.

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, Contract No. DE-FG02-84ER4570. One of us (W.Y.C.) wishes to thank Dr. D. D. Koelling for several discussions and advice.

APPENDIX

Following the same notation as in Ref. 6, we depict the vector relationship of various direct-space points relevant for the reduction of multicenter integrals in Fig. 3. The following relations can be defined:

$$\alpha_T = \alpha_1 + \alpha_2 + \alpha_3 \;, \tag{A1}$$

$$\mathbf{D} = (\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B})/(\alpha_1 + \alpha_2) \;, \tag{A2}$$

$$\mathbf{E} = (\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B} + \alpha_3 \mathbf{C})/\alpha_T \;, \tag{A3}$$

$$\mathbf{F} = [\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B} - (\alpha_1 + \alpha_2)\mathbf{C}]/\alpha_T \;, \tag{A4}$$

$$\vec{\mathrm{AE}} = \mathbf{E} - \mathbf{A};\ \ \vec{\mathrm{AE}} = |\mathbf{E} - \mathbf{A}|, \text{ etc. } , \tag{A5}$$

$$\mathbf{r}_A = \mathbf{r} - \mathbf{A} = \mathbf{r}_E + \vec{\mathrm{AE}}, \text{ etc. } , \tag{A6}$$

$$\alpha_1 \vec{\mathrm{AE}} + \alpha_2 \vec{\mathrm{BE}} + \alpha_3 \vec{\mathrm{CE}} = \mathbf{0} \;. \tag{A7}$$

The three types of integrals involving f orbital $xyze^{-\alpha r^2}$ are obtained as follows:

(A) First type of integral:

$$\langle (x-A_x)(y-A_y)(z-A_z)e^{-\alpha_1 r_A^2} | -\nabla^2 | (x-B_x)(y-B_y)(z-B_z)e^{-\alpha_2 r_B^2} \rangle$$

$$= \frac{1}{2\alpha_2} \frac{\partial}{\partial B_z} \langle (x-A_x)(y-A_y)(z-A_z)e^{-\alpha_1 r_A^2} | -\nabla^2 | (x-B_x)(y-B_y)e^{-\alpha_2 r_B^2} \rangle = \Delta F_1 (F_2 + F_3 + F_4 + F_5) \;,$$

where

$$F_1 = -\eta^4 \zeta^{3/2} e^{-\eta(\mathbf{r}_B - \mathbf{r}_A)^2} \;,$$

$$F_2 = -9 + 22\eta(\vec{\mathrm{AB}})^2 \;,$$

$$F_3 = -4\eta^2(\vec{\mathrm{AB}})^4 \;,$$

$$F_4 = \eta^2[8\eta(\vec{\mathrm{AB}})^2 - 52][(|\vec{\mathrm{AB}}|)_x^2(|\vec{\mathrm{AB}}|)_y^2 + (|\vec{\mathrm{AB}}|)_y^2(|\vec{\mathrm{AB}}|)_z^2 + (|\vec{\mathrm{AB}}|)_z^2(|\vec{\mathrm{AB}}|)_x^2] \;,$$

$$F_5 = \eta^3[120 - 16\eta(\vec{\mathrm{AB}})^2](|\vec{\mathrm{AB}}|)_x^2(|\vec{\mathrm{AB}}|)_y^2(|\vec{\mathrm{AB}}|)_z^2 \;,$$

$$\Delta = \frac{1}{8\alpha_1^3\alpha_2^3},\ \eta = \frac{\alpha_1\alpha_2}{\alpha_1 + \alpha_2},\ \zeta = \frac{\pi}{\alpha_1 + \alpha_2} \;.$$

(B) Second type of integral:

$$\left\langle (x-A_x)(y-A_y)(z-A_z)e^{-\alpha r_A^2} \left\| \left(\frac{1}{r_C}\right) e^{-\alpha_3 r_C^2} \right| (x-B_x)(y-B_y)(z-B_z)e^{-\alpha_2 r_B^2} \right\rangle$$

$$= \frac{1}{2\alpha_2} \frac{\partial}{\partial B_z} \left\langle (x-A_x)(y-A_y)(z-A_z)e^{-\alpha r_A^2} \left\| \left(\frac{1}{r_C}\right) e^{-\alpha_3 r_C^2} \right| (x-B_x)(y-B_y)e^{-\alpha_2 r_B^2} \right\rangle$$

$$= \left(\frac{2\pi}{\alpha_T}\right) \rho (S_0 G_1 - S_2 G_2 + S_4 G_3 - S_6 G_4 + S_8 G_5 - S_{10} G_6 + S_{12} G_7) \;,$$

where $S_n = \int_0^1 t^n e^{-\xi t^2}\, dt$ is evaluated in terms of error functions and

$$G_1 = (|\vec{\mathrm{BE}}|)_z (|\vec{\mathrm{AE}}|)_z \lambda_1 + 0.5\lambda_1/\alpha_T \;,$$

$$G_2 = F_z(|\vec{\mathrm{AE}}|)_z \lambda_1 + (|\vec{\mathrm{BE}}|)_z[\lambda_1 F_z + \lambda_2(|\vec{\mathrm{AE}}|)_1] + 0.5(\lambda_1 + \lambda_2)/\alpha_T \;,$$

$$G_3 = F_z[\lambda_1 F_z + \lambda_2(|\vec{\mathrm{AE}}|)_z] + (|\vec{\mathrm{BE}}|)_z[\lambda_2 F_z + \lambda_3(|\vec{\mathrm{AE}}|)_z] + 0.5(\lambda_2 + \lambda_3)/\alpha_T \;,$$

$$G_4 = F_z[\lambda_2 F_z + \lambda_3(|\vec{\mathrm{AE}}|)_z] + (|\vec{\mathrm{BE}}|)_z[\lambda_3 F_z + \lambda_4(|\vec{\mathrm{AE}}|)_z] + 0.5(\lambda_3 + \lambda_4)/\alpha_T \;,$$

$$G_5 = F_z[\lambda_3 F_z + \lambda_4(|\vec{\mathrm{AE}}|)_z] + (|\vec{\mathrm{BE}}|)_z[\lambda_4 F_z + (|\vec{\mathrm{AE}}|)_z F_x^2 F_y^2] + 0.5(\lambda_4 + F_x^2 F_y^2)/\alpha_T \;,$$

$$G_6 = F_z[\lambda_4 F_z + (|\vec{\mathrm{AE}}|)_z F_x^2 F_y^2] + (|\vec{\mathrm{BE}}|)_z F_z F_x^2 F_y^2 + 0.5 F_x^2 F_y^2/\alpha_T \;,$$

$$G_7 = F_x^2 F_y^2 F_z^2 \;,$$

$$\lambda_1 = [(|\vec{\mathrm{AE}}|)_x(|\vec{\mathrm{BE}}|)_x + 0.5/\alpha_T][(|\vec{\mathrm{AE}}|)_y(|\vec{\mathrm{BE}}|)_y + 0.5/\alpha_T] \;,$$

$$\lambda_2 = [(|\vec{\mathrm{AE}}|)_x F_x + (|\vec{\mathrm{BE}}|)_x F_x + 0.5/\alpha_T][(|\vec{\mathrm{AE}}|)_y(|\vec{\mathrm{BE}}|)_y + 0.5/\alpha_T] + [(|\vec{\mathrm{AE}}|)_x(|\vec{\mathrm{BE}}|)_x + 0.5/\alpha_T]$$
$$\times [(|\vec{\mathrm{AE}}|)_y F_y + (|\vec{\mathrm{BE}}|)_y F_y + 0.5/\alpha_T] \;,$$

$$\lambda_3 = [(|\vec{\mathrm{AE}}|)_x F_x + (|\vec{\mathrm{BE}}|)_x F_x + 0.5/\alpha_T][(|\vec{\mathrm{AE}}|)_y(|\vec{\mathrm{BE}}|)_y F_y^2 + 0.5/\alpha_T] + [(|\vec{\mathrm{AE}}|)_x(|\vec{\mathrm{BE}}|)_x + 0.5/\alpha_T] F_y^2$$
$$+ [(|\vec{\mathrm{AE}}|)_y(|\vec{\mathrm{BE}}|)_y + 0.5/\alpha_T] F_x^2 \;,$$

$$\lambda_4=[(|\vec{\mathrm{AE}}|)_x F_x+(|\vec{\mathrm{BE}}|)_x F_x+0.5/\alpha_T]F_y^2+[(|\vec{\mathrm{AE}}|)_y F_y+(|\vec{\mathrm{BE}}|)_y F_y+0.5/\alpha_T]F_x^2 \ ,$$

$$\rho=\exp(-\alpha_1 A^2-\alpha_2 B^2-\alpha_3 C^2+\alpha_T E^2);\quad \xi=\alpha_T F^2 \ .$$

(C) Third type of integral:

$$\langle (x-A_x)(y-A_y)(z-A_z)e^{-\alpha_1 r_A^2}|e^{-\alpha_3 r_C^2}|(x-B_x)(y-B_y)(z-B_z)e^{-\alpha_2 r_B^2}\rangle$$
$$=\left(\frac{\pi}{\alpha_T}\right)^{3/4}\rho[0.5/\alpha_T+(|\vec{\mathrm{AE}}|)_x(|\vec{\mathrm{BE}}|)_x][0.5/\alpha_T+(|\vec{\mathrm{AE}}|)_y(|\vec{\mathrm{BE}}|)_y][0.5/\alpha_T+(|\vec{\mathrm{AE}}|)_z(|\vec{\mathrm{BE}}|)_z]$$

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[*] Present address: Department of Physics, Chinese University of Science and Technology, Hefei, Anhui, People's Republic of China.

[†] Author to whom correspondence should be addressed.

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