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Hartree-Fock formalism for solids. I. Reciprocal-lattice expansion for the Hartree-Fock exchange term*

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Using the linear-combination-of-atomic-orbitals formalism, the Hartree-Fock (HF) exchange operator has been expressed as a double Fourier integral. In the case of Gaussian basis functions, the Fourier coefficients of the exchange have been calculated analytically in terms of error functions of complex argument. When this Fourier expansion is used to compute matrix elements of the exchange between two Bloch functions, all of the direct lattice sums and the Fourier integral disappear, leaving only a double reciprocal-lattice sum in the expression for the exchange-matrix element. The convergence of this double Fourier series is comparable to the convergence of the Fourier series for the Coulomb term, which has been previously investigated by the authors. In the double Fourier series for the exchange term, as in the case of the Coulomb term, only the first few Fourier coefficients change significantly from the overlapping atomic potential (OAP) to the self-consistent result, and therefore the number of integrals that need to be stored for the self-consistent iterations is greatly reduced. Thus the double reciprocal-lattice expansion for the exchange term enables one to perform a self-consistent HF calculation for crystals with large atoms if the first iteration can be obtained with the OAP. In the case of the OAP, the number of integrals to be computed in direct space is greatly reduced over the number required in the self-consistent case, and therefore the exchange term can be calculated in direct space for crystals with heavy atoms.

I. INTRODUCTION

In recent years there has been a great deal of interest in calculating exact Hartree-Fock (HF) energy bands rather than $X\alpha$ bands[1] in which the exchange term is replaced by a local density approximation. These recent efforts to treat the HF exchange term exactly have been made possible by the development of new mathematical techniques as well as faster computers. As a result of these new developments, one is no longer forced to approximate the exchange term, but instead one is now in a position to perform an exact, self-consistent HF calculation.

The HF calculation is very important in determining the electronic properties of solids for several reasons. First of all, the crystalline HF calculation gives good ground-state properties such as charge densities,[2] Compton profiles, and bulk modulus.[3] Secondly and most important, the HF energy-band calculation provides an exact and known starting point to which correlation corrections can be added in order to obtain accurate excitation properties of crystals. The HF calculation corresponds to the first term in a many-body perturbation series,[4,5] so that once the HF energy bands have been obtained, one knows exactly what has already been included in the calculation and exactly what additional perturbation terms need to be added in order to improve the accuracy of the excitation energies. This is in sharp contrast to $X\alpha$ calculations. Once the exchange term has been replaced by an $X\alpha$ approximation, one cannot go any further to improve the accuracy of the energies because one has no way of knowing what has already been included in the calculation or what additional terms need to be added.

It is well known that HF calculations yield energy differences that are too large, so that correlation corrections need to be added to HF energies in order to obtain more favorable agreement with experiment. One of us has developed a correlation technique, called the screened-exchange-plus-Coulomb-hole (SECH) method,[5,6] which yields close agreement with experiment for the top of the valence band. For example, when the SECH calculation was done for diamond, values of 5.6 and 7.6 eV were obtained for the indirect and direct band gaps, compared with experimental values of 5.6 and 7.4 eV, respectively. The agreement is best for the indirect gap which is the only piece of "hard" experimental information available for diamond. Thus one can obtain accurate excitation energies with the SECH method if one is able to calculate a set of exact HF energy bands to use as a starting point.

Recent attempts to perform exact crystalline HF calculations have been made by Euwema *et al.*[2,7,8] using the direct-space method, by Harris *et al.*[9-11] using reciprocal-space techniques, and by Kunz *et al.*[12] using a localized-orbital method. While Euwema and Harris have carried out HF calculations for crystals containing s and p electrons, such as Li, LiF, and diamond, their formalisms involve so may integrals that it is impractical to apply them to crystals with d electrons. In the case of Kunz's method, the local-orbital techniques have been applied to insulators in which the electrons are tightly bound, however, this method is not easily adapted to semiconductors and metals in which the electronic states are more extended. Thus, what is needed is a generally applicable HF formalism in which the number of integrals to be calculated and stored is reduced to a manageable amount.

The two terms in the HF calculation that present difficulties in terms of number of integrals to be handled are the Coulomb and exchange terms. In the case of the linear-combination-of-atomic-orbitals (LCAO) procedure, which is the method used in this paper, the Coulomb term has been put into a manageable form by expanding the Coulomb potential in a Fourier series in reciprocal-lattice vectors.[13-15] When this is done, the infinite sum of positive and negative charges is included in the $\vec{K}=0$ coefficient, eliminating the complicated and lengthy calculation that would be required to do this sum in direct space. Also, once the first iteration has been obtained using the overlapping atomic potential (OAP), only the first few Fourier coefficients change significantly in the successive iterations required to reach self-consistency, and thus the number of integrals that need to be stored for these iterations is much smaller than in the case of the direct-space calculation. One is still faced with the problem of obtaining convergence of the reciprocal-lattice sum in the first iteration. However, we have developed Ewald techniques[16] which greatly speed up the convergence of this Fourier series so that the first iteration can be obtained in a relatively short time.

It is desirable to handle the exchange term in a similar manner so that the full HF calculation can be done for crystals with heavy atoms. If the exchange term is computed in direct space, then, as in the case of the Coulomb term, the number of integrals to be stored is prohibitive for crystals with d electrons. To overcome this difficulty, we have developed a method for expanding the exchange term in a double Fourier series in reciprocal-lattice vectors. When this is done, then, as in the case of the Coulomb term, only the first few terms in the Fourier series change significantly in the self-consistent iterations, and thus the number of integrals to be stored is greatly reduced. The advantage of the reciprocal-lattice expansion is that it picks out the parts of the Coulomb and exchange terms that change significantly from the first to the final iteration, and thereby greatly reduces the number of integrals that need to be stored for these iterations.

In order for this reciprocal-lattice expansion of the exchange term to be useful in performing a self-consistent HF calculation, it is necessary to obtain the first iteration exchange using the OAP. We have developed a method for calculating the OAP exchange term in direct space by making use of the POLYATOM integral package[17] which computes two-electron integrals containing s, p, and d functions. In the case of the OAP, the number of integrals to be computed in direct space is greatly reduced over the number required in the self-consistent case where the wave function is a linear combination of Bloch functions. Also none of the direct-space integrals needs to be stored since self-consistency is achieved using the reciprocal-lattice expansion. Thus if the first iteration exchange is computed using the OAP, then, a direct-space calculation is feasible for crystals with large atoms.

It should be noted that the reciprocal-space procedure of Harris *et al.* is substantially different from the method presented in this paper. In the Harris method, only the bare Coulomb interaction is written as a single Fourier integral, while in the method given here the entire exchange operator is expressed as a double Fourier integral, which enables the exchange-matrix element to be written as a double sum over reciprocal-lattice vectors.

II. RECIPROCAL-LATTICE EXPANSION FOR EXCHANGE TERM

In the LCAO method, the HF exchange operator is given by

$$V_{\mathrm{ex}}(\vec{r}_1,\vec{r}_2)=-\rho(\vec{r}_1,\vec{r}_2)v(\vec{r}_1,\vec{r}_2), \tag{2.1}$$

$$v(\vec{r}_1,\vec{r}_2)=e^2/|\vec{r}_1-\vec{r}_2|, \tag{2.2}$$

$$\rho(\vec{r}_1,\vec{r}_2)=\sum_{\vec{k},l\ \mathrm{occ.}} u^*_{\vec{k}l}(\vec{r}_2)u_{\vec{k}l}(\vec{r}_1), \tag{2.3}$$

$$u_{\vec{k}l}(\vec{r})=\sum_i b_{li}(\vec{k})\psi_{\vec{k}i}(\vec{r}), \tag{2.4}$$

$$\psi_{\vec{k}i}(\vec{r})=\frac{1}{\sqrt{N}}\sum_\nu e^{i\vec{k}\cdot\vec{R}_\nu}\phi_i(\vec{r}-\vec{R}_\nu), \tag{2.5}$$

where the $u_{\vec{k}l}$ are one-electron states, the ϕ_i are atomic orbitals, the $\psi_{\vec{k}i}$ are the Bloch functions associated with the atomic orbitals, the b_{li} are the coefficients of the Bloch functions, $\vec{k}$ is a reciprocal-space vector restricted to the first Brillouin zone, l is a band index, the $\vec{R}_\nu$ are direct-lattice vectors, and N is the number of unit-cells in the crystal.

The exchange operator can be written as a double Fourier integral as follows:

$$V_{\mathrm{ex}}(\vec{r}_1,\vec{r}_2)=\int V'_{\mathrm{ex}}(\vec{q}_1,\vec{q}_2) \times e^{i\vec{q}_1\cdot\vec{r}_1-i\vec{q}_2\cdot\vec{r}_2}\,d\vec{q}_1\,d\vec{q}_2, \tag{2.6}$$

where

$$V'_{\mathrm{ex}}(\vec{q}_1,\vec{q}_2)=\frac{1}{(2\pi)^6}\int V_{\mathrm{ex}}(\vec{r}_1,\vec{r}_2)\times e^{-i\vec{q}_1\cdot\vec{r}_1+i\vec{q}_2\cdot\vec{r}_2}\,d\vec{r}_1\,d\vec{r}_2. \tag{2.7}$$

Then using the expression for V_{ex} given by Eqs. (2.1)–(2.5), Eq. (2.7) becomes

$$V'_{\mathrm{ex}}(\vec{q}_1,\vec{q}_2)=\sum_{\vec{K}_2} V_{\mathrm{ex}}(\vec{q}_1,\vec{q}_2)\,\delta(\vec{q}_2-\vec{q}_1-\vec{K}_2), \tag{2.8}$$

$$V_{\mathrm{ex}}(\vec{q}_1,\vec{q}_2)=-\frac{e^2}{(2\pi)^3\Omega}\times\sum_{ij\nu}A_{ij\nu}\int\frac{\phi_i^*(\vec{r}_2)\phi_j(\vec{r}_1-\vec{R}_\nu)}{|\vec{r}_1-\vec{r}_2|}\times e^{-i\vec{q}_1\cdot\vec{r}_1+i\vec{q}_2\cdot\vec{r}_2}\,d\vec{r}_1\,d\vec{r}_2, \tag{2.9}$$

$$A_{ij\nu}=\frac{1}{N}\sum_{\vec{k}l} b_{li}^*(\vec{k})\,b_{lj}(\vec{k})\,e^{i\vec{k}\cdot\vec{R}_\nu}, \tag{2.10}$$

where $\vec{K}_2$ is a reciprocal lattice vector, Ω is the volume of the unit cell, and we have used the relationship

$$\sum_{\nu} e^{i(\vec{q}_2-\vec{q}_1)\cdot\vec{R}_\nu}=\frac{(2\pi)^3}{\Omega}\sum_{\vec{K}_2}\delta(\vec{q}_2-\vec{q}_1-\vec{K}_2). \tag{2.11}$$

Putting (2.8) into (2.6), we can then express the exchange operator in terms of a Fourier integral and reciprocal lattice sum

$$V_{\mathrm{ex}}(\vec{r}_1,\vec{r}_2)=\sum_{\vec{K}_2}\int V_{\mathrm{ex}}(\vec{q},\vec{q}+\vec{K}_2)\times e^{i\vec{q}\cdot\vec{r}_1-i(\vec{q}+\vec{K}_2)\cdot\vec{r}_2}\,d\vec{q}. \tag{2.12}$$

If ϕ_i and ϕ_j are both s Gaussian orbitals, then the integral in Eq. (2.9) if of the form

$$I=\int\frac{\exp[-\alpha_i(\vec{r}_2-\vec{A})^2-\alpha_j(\vec{r}_1-\vec{B})^2]}{|\vec{r}_1-\vec{r}_2|}\times e^{-i\vec{q}_1\cdot\vec{r}_1+i\vec{q}_2\cdot\vec{r}_2}\,d\vec{r}_1\,d\vec{r}_2, \tag{2.13}$$

where ϕ_i and ϕ_j are centered on the sites $\vec{A}$ and $\vec{B}$, respectively. In order to obtain the integral in (2.9) when ϕ_i and ϕ_j are p or d Gaussian orbitals, one can take derivatives of I with respect to $\vec{A}$ and $\vec{B}$. Thus the basic integral that needs to be done is the one given in Eq. (2.13).

This integral can be put in the form

$$I=\frac{\pi^{3/2}}{(\alpha_i+\alpha_j)^{3/2}}\exp\left(-i\vec{q}_1\cdot\vec{B}+i\vec{q}_2\cdot\vec{A}+i\vec{K}\cdot\vec{C}-\frac{(\vec{q}_2-\vec{q}_1)^2}{4(\alpha_i+\alpha_j)}\right)\times\int\frac{1}{r}\exp[-i\vec{K}\cdot\vec{r}-\alpha(\vec{r}-\vec{C})^2]\,d\vec{r}, \tag{2.14}$$

where

$$\vec{C}=\vec{B}-\vec{A}, \tag{2.15}$$

$$\vec{K}=\frac{\alpha_i}{\alpha_i+\alpha_j}\vec{q}_1+\frac{\alpha_j}{\alpha_i+\alpha_j}\vec{q}_2, \tag{2.16}$$

$$\alpha=\frac{\alpha_i\alpha_j}{\alpha_i+\alpha_j}. \tag{2.17}$$

It now remains to do the integral given in Eq. (2.14),

$$J=\int\frac{1}{r}\exp[-i\vec{K}\cdot\vec{r}-\alpha(\vec{r}-\vec{C})^2]\,d\vec{r}. \tag{2.18}$$

This integral will be evaluated in this section in a simplified manner. A rigorous evaluation of the integral is given in the Appendix. Completing the square in (2.18), we have

$$J=\exp\left(-i\vec{K}\cdot\vec{C}-\frac{K^2}{4\alpha}\right)\times\int\frac{1}{r}\exp\left[-\alpha\left(\vec{r}+i\frac{\vec{D}}{\alpha^{1/2}}\right)^2\right]d\vec{r}, \tag{2.19}$$

where $\vec{D}$ is a complex vector given by

$$\vec{D}=\vec{K}/2\alpha^{1/2}+i\alpha^{1/2}\vec{C}. \tag{2.20}$$

Since there is no preferred direction in the integral in (2.19), the result of the integration must depend only on the magnitude of $\vec{D}$, which is defined by

$$D=(\vec{D}\cdot\vec{D})^{1/2}. \tag{2.21}$$

If we evaluate this integral for the special case that $\vec{K}\parallel\vec{C}$, then we can determine how the integral depends on the magnitude of $\vec{D}$, and this result will then be true for the general case when $\vec{K}$ and $\vec{C}$ are not parallel.

If $\vec{K}\parallel\vec{C}$, we can carry out the integration in (2.19) to obtain

$$J=\frac{2\pi}{\alpha}\exp(-i\vec{K}\cdot\vec{C}-K^2/4\alpha)\,\frac{\mathrm{erf}(iD)}{iD}, \tag{2.22}$$

where the error function is defined by

$$\mathrm{erf}(z)=\int_0^z e^{-t^2}\,dt. \tag{2.23}$$

Putting (2.22) into (2.14), we have

$$I=\frac{2\pi^{5/2}}{\alpha_i\alpha_j(\alpha_i+\alpha_j)^{1/2}}\times\exp\left(-i\vec{q}_1\cdot\vec{B}+i\vec{q}_2\cdot\vec{A}-\frac{q_1^2}{4\alpha_j}-\frac{q_2^2}{4\alpha_i}\right)\frac{\mathrm{erf}(iD)}{iD}. \tag{2.24}$$

Since for $\arg z>\frac{1}{4}\pi$, $\mathrm{erf}(z)\to\infty$ as $z\to\infty$, it is more convenient to express I in terms of the well-behaved function w:

$$I=\frac{\pi^3}{\alpha_i\alpha_j(\alpha_i+\alpha_j)^{1/2}}\,\frac{\exp(-i\vec{q}_1\cdot\vec{B}+i\vec{q}_2\cdot\vec{A})}{iD}$$
$$\times\left[\exp\left(-\alpha C^2+i\vec{K}\cdot\vec{C}-\frac{(\vec{q}_2-\vec{q}_1)^2}{4(\alpha_i+\alpha_j)}\right)w(D)\right.$$
$$\left.-\exp\left(-\frac{q_1^2}{4\alpha_j}-\frac{q_2^2}{4\alpha_i}\right)\right], \tag{2.25}$$

where

$$w(z)=e^{-z^2}\left(1+i\frac{2}{\pi^{1/2}}\int_0^z e^{t^2}\,dt\right). \tag{2.26}$$

In the case that ϕ_i and ϕ_j are p or d functions, the integral in (2.9) can be obtained by taking derivatives of (2.25) with respect to $\vec{A}$ and $\vec{B}$.

III. EXCHANGE-MATRIX ELEMENTS

In order to perform a Hartree-Fock calculation for a crystal, one must compute the matrix elements of the exchange operator with respect to the Bloch functions

$$V_{ij}^{\text{ex}}(\vec{k})=\int\psi_{\vec{k}i}^*(\vec{r}_1)V_{\text{ex}}(\vec{r}_1,\vec{r}_2)\psi_{\vec{k}j}(\vec{r}_2)\,d\vec{r}_1\,d\vec{r}_2. \tag{3.1}$$

Using (2.12), which expresses the exchange operator in terms of a reciprocal-lattice sum and Fourier integral, we can write the exchange-matrix element as

$$V_{ij}^{\text{ex}}(\vec{k})=\sum_{\vec{K}_1,\vec{K}_2}\int V_{\text{ex}}(\vec{q}+\vec{K}_1,\vec{q}+\vec{K}_2)$$
$$\times\psi_{\vec{k}i}^*(\vec{q}+\vec{K}_1)\psi_{\vec{k}j}(\vec{q}+\vec{K}_2)\,d\vec{q}, \tag{3.2}$$

$$\psi_{\vec{k}i}(\vec{q})=\int\psi_{\vec{k}i}(\vec{r})e^{-i\vec{q}\cdot\vec{r}}\,d\vec{r}, \tag{3.3}$$

where the Fourier integral on $\vec{q}$, which was over all of reciprocal space, has been restricted to the first Brillouin zone and a sum over reciprocal-lattice vectors $\vec{K}_1$ has been added.

Using (2.5) and (2.11), one can put (3.3) in the form

$$\psi_{\vec{k}i}(\vec{q})=\frac{1}{\sqrt{N}}\,\frac{(2\pi)^3}{\Omega}\,\phi_i(\vec{q})\delta(\vec{q}-\vec{k}), \tag{3.4}$$

$$\phi_i(\vec{q})=\int\phi_i(\vec{r})e^{-i\vec{q}\cdot\vec{r}}\,d\vec{r}. \tag{3.5}$$

Then putting (3.4) into (3.2) and integrating over $\vec{q}$, we obtain

$$V_{ij}^{\text{ex}}(\vec{k})=\frac{(2\pi)^3}{\Omega}\sum_{\vec{K}_1,\vec{K}_2}V_{\text{ex}}(\vec{k}+\vec{K}_1,\vec{k}+\vec{K}_2)$$
$$\times\phi_i^*(\vec{k}+\vec{K}_1)\phi_j(\vec{k}+\vec{K}_2). \tag{3.6}$$

In the above expression for the exchange-matrix element, both of the direct lattice sums as well as the Fourier integral have disappeared, leaving only a double sum over reciprocal-lattice vectors.

If ϕ_i is an s Gaussian orbital, then the integral in (3.5) is of the form

$$L=\int e^{-\alpha_i(\vec{r}-\vec{A})^2-i\vec{q}\cdot\vec{r}}\,d\vec{r}\ , \tag{3.7}$$

where ϕ_i is centered on the site $\vec{A}$. In order to obtain the integral in (3.5) when ϕ_i is a p or d orbital, one can take derivatives of L with respect to $\vec{A}$. After the expression for the integral has been obtained, $\vec{A}$ is set equal to zero. Carrying out the integration in (3.7), we have

$$L=\frac{\pi^{3/2}}{\alpha_i^{\,3/2}}\,e^{-i\vec{q}\circ\vec{A}-q^2/4\alpha_i}. \tag{3.8}$$

IV. CONVERGENCE OF DOUBLE RECIPROCAL-LATTICE SUM

Now that the exchange-matrix element has been expressed in terms of a double reciprocal-lattice sum, one needs to examine the convergence of this double sum. For the case of Gaussian orbitals, this convergence can be studied by comparing it to the convergence of the single reciprocal-lattice sum in the Coulomb term, which has been thoroughly investigated by the authors.[15,16] When the Coulomb potential is expanded in a single reciprocal-lattice sum, the coefficients $V_C(\vec{K}_1)$ can be written as a nuclear part $V_C^{\text{nuc}}(\vec{K}_1)$ plus an electronic part $V_C^{\text{el}}(\vec{K}_1)$

$$V_C(\vec{K}_1)=V_C^{\text{nuc}}(\vec{K}_1)+V_C^{\text{el}}(\vec{K}_1). \tag{4.1}$$

The nuclear part of the coefficient depends on $1/K_1^2$ while the electronic part depends on $1/K_1^2$ times exponentials of the form $e^{-K_1^2/4(\alpha_i+\alpha_j)}$. For p and d functions there are other factors present in the electronic part of the coefficient; however, the major factor that determines convergence is the exponential in K_1^2.

In the energy-band calculation, one does not need to compute the Coulomb potential by itself, but rather matrix elements of the Coulomb potential, and these matrix elements contribute additional convergence factors of the form $e^{-K_1^2/4(\alpha_i+\alpha_j)}$ to both the nuclear and electronic terms. In the case of the nuclear term, the major convergence factor comes from the matrix element rather than from the nuclear potential itself, since the $1/K_1^2$ factor produces negligible convergence compared to the exponential in K_1^2.

In the case of the double sum in the exchange term, the matrix element produces convergence factors of the form $e^{-(\vec{k}+\vec{K}_1)^2/4\alpha_i}$ for both the $\vec{K}_1$ and the $\vec{K}_2$ sums, as shown by Eqs. (3.6) and (3.8). Thus the convergence factors that come from the matrix elements are of the same form for all of the sums involved in the Coulomb and exchange terms.

Since the contributions of the matrix elements are the same, then the relative convergence of the Coulomb and exchange sums can be determined by a comparison of the Coulomb and exchange coefficients. In order to examine the convergence factors in the exchange coefficient, it is convenient to replace the $\vec{K}_1$ and $\vec{K}_2$ sums by sums over $\vec{K}_2-\vec{K}_1$ and $\vec{K}_2+\vec{K}_1$. Then in the first term in brackets in Eq. (2.25), which is the dominant term, there is an exponential in $(\vec{K}_2-\vec{K}_1)^2$, $e^{-(\vec{K}_2-\vec{K}_1)^2/4(\alpha_i+\alpha_j)}$, and a term $w(D)/iD$ which goes as $1/K^2$ for large $\vec{K}$. Since $\vec{K}=\vec{k}+[1/(\alpha_i+\alpha_j)](\alpha_i\vec{K}_1+\alpha_j\vec{K}_2)$, the $w(D)/iD$ term produces a convergence factor of the form $[1/(\vec{K}_2+\vec{K}_1)^2]$. Thus the $\vec{K}_2+\vec{K}_1$ sum and the $\vec{K}_2-\vec{K}_1$ sum have convergence factors similar to those of the nuclear and electronic parts of the Coulomb term, respectively. Therefore, one of the sums in the exchange term converges like the nuclear part of the Coulomb term, while the other sum converges like the electronic part of the Coulomb term.

V. SELF-CONSISTENT HF CALCULATION

The authors have thoroughly studied the convergence of the reciprocal-lattice sums in the nuclear and electronic parts of the Coulomb term, and have developed techniques to obtain rapid convergence in both cases.[15,16] However, since each of these sums contains a large number of terms when converged, a substantial amount of time would probably be required to achieve convergence of the double sum. Thus it would probably not be feasible to obtain convergence of the double reciprocal-lattice sum for the full exchange term. However, when performing a self-consistent HF calculation, it is not necessary to converge the double sum for the full exchange term if one computes the first iteration using the overlapping atomic potential (OAP).

In both the Coulomb and exchange reciprocal-lattice sums, the large number of terms is required to describe the rapidly varying charge density of the core electrons, while only the first few terms in the sum are needed to describe the slowly varying charge density of the valence electrons. In going from the OAP to self-consistency, the core density is virtually unchanged while the valence charge density changes appreciably. Therefore only the first few coefficients in the sum change significantly in the iterations required to reach self-consistency. Thus if $\Delta V_{ij}^{\text{ex}}$ is defined as the change in the exchange-matrix element from the OAP to the self-consistent case, then the double reciprocal-lattice sum for $\Delta V_{ij}^{\text{ex}}$ converges after only a few terms.

Since the double sum for $\Delta V_{ij}^{\text{ex}}$ converges rapidly, it can be used to achieve self-consistency once the first iteration has been obtained with the OAP. In order to calculate $\Delta V_{ij}^{\text{ex}}$, one needs to compute the exchange coefficient for the OAP case. In the case of the OAP, the exchange operator has the form

$$V_{\text{ex}}^{\text{OAP}}(\vec{r}_1,\vec{r}_2)=-\frac{e^2}{|\vec{r}_1-\vec{r}_2|}\sum_{i\nu}\phi_i^*(\vec{r}_2-\vec{R}_\nu)\phi_i(\vec{r}_1-\vec{R}_\nu), \tag{5.1}$$

and this leads to the following expression for the exchange coefficient:

$$V_{\text{ex}}^{\text{OAP}}(\vec{q}_1,\vec{q}_2)=-\frac{e^2}{(2\pi)^3\Omega}\sum_i\int\frac{\phi_i^*(\vec{r}_2)\phi_i(\vec{r}_1)}{|\vec{r}_1-\vec{r}_2|}\times e^{-i\vec{q}_1\cdot\vec{r}_1+i\vec{q}_2\cdot\vec{r}_2}d\vec{r}_1\,d\vec{r}_2. \tag{5.2}$$

Then the change in the exchange-matrix element is given by

$$\Delta V_{ij}^{\text{ex}}(\vec{k})=\frac{(2\pi)^3}{\Omega}\sum_{\vec{K}_1,\vec{K}_2}\Delta V_{\text{ex}}(\vec{k}+\vec{K}_1,\vec{k}+\vec{K}_2)\times\phi_i^*(\vec{k}+\vec{K}_1)\phi_j(\vec{k}+\vec{K}_2), \tag{5.3}$$

$$\Delta V_{\text{ex}}(\vec{q}_1,\vec{q}_2)=V_{\text{ex}}(\vec{q}_1,\vec{q}_2)-V_{\text{ex}}^{\text{OAP}}(\vec{q}_1,\vec{q}_2), \tag{5.4}$$

where V_{ex}, which is defined in Eq. (2.9), is the exchange coefficient in the self-consistent case.

In order for the double reciprocal-lattice sum to be useful in performing a self-consistent HF calculation, it remains to compute the first iteration exchange-matrix elements using the OAP. Before doing this, it is interesting to examine the direct-space expression for the exchange-matrix elements in the self-consistent case, which can be obtained by putting (2.1) into (3.1):

$$V_{ij}^{\text{sc}}(\vec{k})=-e^2\sum_\nu e^{i\vec{k}\cdot\vec{R}_\nu}\sum_{mn\nu'\nu''}A_{mn\nu\nu''\nu''}\int\phi_i^*(\vec{r}_1)\frac{\phi_m^*(\vec{r}_2-\vec{R}_{\nu'}-\vec{R}_\nu)\phi_n(\vec{r}_1-\vec{R}_{\nu''})}{|\vec{r}_1-\vec{r}_2|}\phi_j(\vec{r}_2-\vec{R}_\nu)\,d\vec{r}_1\,d\vec{r}_2, \tag{5.5}$$

$$A_{mn\nu'\nu}=\frac{1}{N}\sum_{k',l'\ \text{occ.}}b_{l'm}^*(\vec{k}')b_{l'n}(\vec{k}')e^{i\vec{k}'\cdot(\vec{R}_{\nu''}-\vec{R}_{\nu'}-\vec{R}_\nu)}, \tag{5.6}$$

where the integrals given in (5.5) are two-electron integrals.

The above expression has been written out in detail in order to demonstrate some of the difficulties that it presents. In addition to the sums over Brillouin zone points and bands, there are three direct lattice sums and two sums over atomic orbitals. Since the matrix elements must be calculated for each pair of orbitals ϕ_i, ϕ_j, then when one considers the total number of matrix elements to be computed, there are actually four sums over orbitals. Thus the total number of integrals to be computed depends on the fourth power of the number of orbitals. As a result of the three direct lattice sums and four sums over orbitals, the total number of integrals quickly becomes unmanageable as the size of the atoms increases, and therefore it would not be feasible to compute the above matrix elements for crystals containing *d* electrons.

However, in the case of the OAP, where the one-electron wave function is a single atomic orbital rather than a linear combination of Bloch functions, the exchange-matrix elements in direct space have a simpler form. Putting (5.1) into (3.1), one obtains the expression for these matrix elements:

$$V_{ij}^{\mathrm{OAP}}(\vec{k}) = -e^2 \sum_{\nu} e^{i\vec{k}\cdot\vec{R}_\nu} \sum_{m\nu'} \int \phi_i^*(\vec{r}_1) \frac{\phi_m^*(\vec{r}_2 - \vec{R}_{\nu'})\phi_m(\vec{r}_1 - \vec{R}_{\nu'})}{|\vec{r}_1 - \vec{r}_2|} \phi_j(\vec{r}_2 - \vec{R}_\nu)\, d\vec{r}_1\, d\vec{r}_2. \tag{5.7}$$

The above expression, which contains only two direct lattice sums and one sum over orbitals, is considerably simpler than the expression for the matrix elements in the self-consistent case. Thus in the case of the OAP, the number of integrals to be calculated is greatly reduced, and therefore it is feasible to compute the exchange-matrix elements in direct space for crystals with large atoms.

In order to obtain the integrals involved in the direct-space OAP calculation, we have made use of the POLYATOM computer program[17] which calculates two-electron integrals containing *s*, *p*, and *d* functions.

In order to perform a self-consistent HF calculation, one must compute the Coulomb and exchange-matrix elements for each of the iterations required to reach self-consistency. The self-consistent procedures for the Coulomb term have been thoroughly discussed in previous papers by the authors.[14,15] In order to handle the exchange term in a self-consistent HF calculation, one first uses the OAP to compute the first iteration exchange-matrix elements in direct space, according to Eq. (5.7). After the first-iteration wave functions have been obtained, one computes the change in the exchange-matrix elements from the OAP to the self-consistent case, as given by (5.3). The changes in the matrix elements are then added to the original OAP matrix elements to give new exchange-matrix elements which are used in the next iteration. This process is continued until self-consistency is reached.

VI. APPLICATION TO CRYSTALS WITH *d* ELECTRONS

One of the most important features of the method described above is that it can be applied to crystals containing *d* electrons, since the double reciprocal-lattice expansion does not depend strongly on the number of atomic orbitals. As indicated in Sec. V, when the crystal contains heavy atoms, ther a direct-space calculation is feasible only in the case of the OAP. In the self-consistent case, the direct-space calculation would require a prohibitive amount of time for crystals with large atoms, since the number of integrals to be computed goes as the fourth power of the number of atomic orbitals. However, in the case of the double reciprocal-lattice expansion for the exchange term, the number of integrals to be computed depends on only the second power of the number of orbitals, as shown by Eq. (2.9). There are also two atomic orbitals in the expression for the exchange-matrix elements; these are not involved in the integrals in Eq. (2.9). Thus the double reciprocal-lattice expansion is not strongly dependent on the number of orbitals, and therefore the method presented in this paper can be successfully applied to crystals with *d* electrons.

Applications of this method are given in the second paper of this series.

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APPENDIX

It is desired to evaluate the integral

$$I_1 = \int \frac{1}{r} e^{-i\vec{K}\cdot\vec{r} - \alpha(\vec{r} - \vec{C})^2} d\vec{r}. \tag{A1}$$

Picking the *z* axis along $\vec{C}$ and rotating the *x* axis so that $\vec{K}$ lies in the *xz* plane, one obtains

$$I_1 = 2\pi \int \frac{1}{r} e^{-\alpha r^2 - \alpha C^2} r^2 \, dr I_2, \tag{A2}$$

$$I_2 = \int_0^{\pi} e^{-iKr\cos\theta_K \cos\theta + 2\alpha r C \cos\theta} \times J_0(Kr\sin\theta_K \sin\theta) \sin\theta \, d\theta. \tag{A3}$$

In the interval $(0,\pi)$, the integrand in (A3) can be written as an even part and an odd part about the point $\theta = \frac{1}{2}\pi$. Then I_2 is equal to twice the integral of the even part from 0 to $\frac{1}{2}\pi$:

$$I_2 = 2\int_0^{\pi/2} \cos(\beta\cos\theta) \, J_0(\sigma\sin\theta)\sin\theta \, d\theta, \tag{A4}$$

$$\beta = Kr\cos\theta_K + i2\alpha r C, \tag{A5}$$

$$\sigma = Kr\sin\theta_K. \tag{A6}$$

Evaluating this integral, we have[18]

$$I_2 = \frac{2^{1/2}\pi^{1/2}}{(\sigma^2+\beta^2)^{1/4}} J_{1/2}((\sigma^2+\beta^2)^{1/2}), \tag{A7}$$

$$= 2\,\frac{\sin(2\alpha^{1/2}Dr)}{2\alpha^{1/2}Dr}, \tag{A8}$$

where

$$D = (\vec{D}\cdot\vec{D})^{1/2}, \tag{A9}$$

$$\vec{D} = \vec{K}/2\alpha^{1/2} + i\alpha^{1/2}\vec{C}. \tag{A10}$$

Using (A8), (A2) becomes

$$I_1 = \frac{2\pi}{\alpha^{1/2}D} e^{-\alpha C^2} I_3, \tag{A11}$$

$$I_3 = \int_0^{\infty} e^{-\alpha r^2} \sin(2\alpha^{1/2}Dr) \, dr. \tag{A12}$$

Carrying out the integration in (A12), we obtain an error function of complex argument,

$$I_3 = \frac{1}{i\alpha^{1/2}} e^{-D^2} \operatorname{erf}(iD), \tag{A13}$$

$$\operatorname{erf}(z) = \int_0^{z} e^{-t^2} \, dt. \tag{A14}$$

Then putting (A13) into (A11), we have

$$I_1 = \frac{2\pi}{\alpha} e^{-i\vec{K}\cdot\vec{C} - K^2/4\alpha} \frac{\operatorname{erf}(iD)}{iD}. \tag{A15}$$

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