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Convergence of Reciprocal-Lattice Sums: Exact Formulas for the Ewald Method*

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While self-consistent linear-combination-of-atomic orbital energy band calculations are now routinely performed, quantitative results require very careful application of the method, and the novice must be aware of certain pitfalls. This paper discusses one of the difficulties encountered: convergence of lattice sums. These sums are sometimes extremely slow to converge, but may be obtained by the Ewald technique with a reasonable computational effort. This paper presents a set of exact formulas for application of the technique which are not readily available in the literature, and demonstrates the Ewald approach by applying them in a calculation for the LiF crystal.

1. INTRODUCTION

The calculation of electronic energy bands from first principles has been accomplished by several methods, among them the orthogonalized-plane-wave (OPW), the augmented-plane-wave (APW) and the linear-combination-of-atomic-orbitals (LCAO) methods [1]. Each of these methods has special advantages, but conceptual simplicity and the ease with which energy bands may be generated self-consistently throughout the Brillouin zone have stimulated a large number of LCAO studies. While an article as recent as 1971 by a reputable, but uninformed, reviewer [2] dismissed the LCAO method as "impossible ... to describe states in a metal or semiconductor in or above the valence and conduction bands," evidence was available as early as 1966 that, properly applied, the method may be made quantitatively as good as others [3]. A glance through the subheading "LCAO Cal-

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culations" in *Physics Abstracts Subject Index* reveals a remarkable increase in the number of LCAO studies over the past 5 years.

An enormous literature exists in the application of the LCAO method to molecular structure. A number of approximate LCAO theories have been evolved, primarily by chemists, to handle complex molecules, but these theories are not always reliable; when good results are obtained it is often for the wrong reasons. A review article by Nicholson summarizes the situation for molecular studies [4].

Errors which are important in molecular calculations are sometimes of less importance in solid state calculations, but difficulties do arise which are important to solids. Among these problems are (1) linear dependence of Bloch basis functions; (2) proper evaluation of multicentered integrals; (3) convergence of the basis set; (4) evaluation of certain lattice sums.

Because of instabilities produced by small numerical errors in overlap integrals, a near-linear dependence of the LCAO Bloch basis functions may produce negative overlap eigenvalues and/or an extreme sensitivity of certain energy eigenvalues to small errors in the potential energy integrals. Experienced LCAO theorists eliminate or replace the offending basis functions, but usually do not discuss the problem in detail in published results [5]. A general discussion with references to earlier work is given by Ahlenius *et al.* [6].

Proper evaluation of multicentered integrals is required for quantitative LCAO results; it was neglect of certain of these integrals which caused poor results in earlier LCAO studies. Introduction of Gaussian orbitals makes possible accurate evaluation of these integrals. Neglect of multicentered integrals has been investigated in [7, 8, 9]. As a rule they cannot be neglected in quantitative, first-principles work unless great care is taken in estimating their magnitude.

Convergence of LCAO expansions with respect to the choice of basis orbitals has been studied previsouly [10]. It has been found that (depending upon the range of energies desired) solid state LCAO studies may be made without the large number of orbitals necessary for accurate atomic and molecular calculations. Periodic, rather than asymptotic, boundary conditions are thought to be responsible for this simplification. Inclusion of d and f symmetry orbitals permits accurate determination of energies in the higher conduction bands.

It is the purpose of this paper to discuss the fourth difficulty mentioned above—convergence of certain lattice sums. This problem is an old one in theoretical physics and was first encountered in calculations of cohesive energies of ionic solids. Various tricks for doing sums are discussed in the literature and in elementary solid state texts. The best general technique was presented by Ewald [11]. Although this technique has been discussed briefly and applied approximately in another LCAO calculation [12], it has not been used in all LCAO studies. It is the purpose of this paper to give an exposition of the Ewald technique in an LCAO calculation and provide formulas not available in the literature which should be of general use.

2. THE LCAO EQUATIONS

While there is no comprehensive review article of the LCAO method as now practiced, there is a good discussion, with references to the literature, in the text by Callaway [1]. For solid state calculations in perfect crystals, a legitimate LCAO must satisfy Bloch's theorem. This is done by using appropriate phase factors in the LCAO, one possible choice being the Bloch function

$$b_i(\mathbf{k}, \mathbf{r}) = \sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l} \phi_i(\mathbf{r} - \mathbf{R}_l), \tag{1}$$

where ϕ_i is a known atomic orbital or other localized function centered on site $\mathbf{R}_l$, $\mathbf{k}$ is the wave vector, and the sum is over all lattice sites $\mathbf{R}_l$. For convenience we consider a monatomic crystal; if there is more than one atom per lattice site, additional Bloch functions may be constructed which are displaced from $\mathbf{R}_l$ appropriately. Expanding the electron wavefunction in these known Bloch functions, the usual secular equation may be obtained from the Schrödinger equation

$$| H_{ij}(\mathbf{k}) - E(\mathbf{k})\, S_{ij}(\mathbf{k}) | = 0. \tag{2}$$

Here the Hamiltonian matrix elements are given by

$$H_{ij}(\mathbf{k}) = \sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l} \int \phi_i^*(\mathbf{r})\, H\phi_j(\mathbf{r} - \mathbf{R}_l)\, d^3r. \tag{3}$$

The overlap matrix elements $S_{ij}(\mathbf{k})$, may be obtained by replacing H with the identity operator. If the Hartree–Fock equations are to be solved, the Hamiltonian operator must be replaced with the Fock operator. In Hartree–Fock studies, if Gaussian orbitals are used as LCAO basis functions, all multicenter integrals which result may be done. However, direct lattice sums must be carefully evaluated using an Ewald summation method [9]. Since Hartree–Fock solutions are expected to be very expensive and difficult to obtain for heavier elements and compounds, it is likely that the Slater approximation will continue to be used for the exchange term for years to come. Thus, we consider here the Hartree–Fock–Slater approximation.

With the Slater local exchange approximation it is more economical to Fourier analyze the crystal potential, although reciprocal lattice sums which are obtained may also be extremely slow to converge. The potential energy integrals still present difficulty. One way to evaluate these multicentered integrals to a desired degree of accuracy is to use Gaussian- or Slater-type orbitals, ϕ_i, and take advantage of the Fourier transform of the crystal potential

$$V(\mathbf{r}) = \sum_n V(\mathbf{K}_n)\, e^{i\mathbf{K}_n\cdot\mathbf{r}}, \tag{4}$$

where $\mathbf{K}_n$ are reciprocal-lattice vectors. The potential energy term of Eq. (3) becomes

$$V_{ij}(\mathbf{k}) = \sum_{l} e^{i\mathbf{k}\cdot\mathbf{R}_l} V_{ij}(\mathbf{R}_l), \tag{5}$$

where

$$V_{ij}(\mathbf{R}_l) = \sum_{n} V(\mathbf{K}_n)\, E_{ij}(\mathbf{K}_n, \mathbf{R}_l) \tag{6}$$

and

$$E_{ij}(\mathbf{K}_n, \mathbf{R}_l) = \int \phi_i^*(\mathbf{r})\, e^{i\mathbf{K}_n\cdot\mathbf{r}} \phi_j(\mathbf{r} - \mathbf{R}_l)\, d^3r. \tag{7}$$

The integrals $E_{ij}(\mathbf{K}_n, \mathbf{R}_l)$ may be evaluated exactly with Gaussian orbitals, but depending upon the states i and j, the Fourier series may prove intractable, thereby necessitating the use of special techniques to accelerate convergence.

3. THE EWALD PROCEDURE

Three techniques used to accelerate convergence are (1) the Ewald expansion; (2) integration; (3) extrapolation of the Fourier series. The integration technique sums the Fourier series to a maximum K_n and approximates the rest by an integral over the remaining terms [13, 14]. The extrapolation technique is based on the observation that the Fourier sum after N stars is approximately a linear function of $1/N$ [14]. Extrapolation is made to $1/N = 0$, corresponding to a sum over an infinite number of RLV's. By combining the Ewald expansion with the extrapolation technique, a substantial decrease in computational time and more accurate quantitative energy band calculations are possible.

The Fourier transform of the crystal potential is expressed as

$$V(\mathbf{K}_n) = V_{\text{ion}}(\mathbf{K}_n) + V_{\text{el}}(\mathbf{K}_n) + V_{\text{ex}}(\mathbf{K}_n), \tag{8}$$

where $V_{\text{ion}}(\mathbf{K}_n)$ is the ionic part of the coulomb potential, $V_{\text{el}}(\mathbf{K}_n)$ is the electronic part of the coulomb potential, and $V_{\text{ex}}(\mathbf{K}_n)$ is the Fourier transform of the exchange potential.

The convergence rate of the sum in Eq. (6) depends upon both $V(\mathbf{K}_n)$ and $E_{ij}(\mathbf{K}_n, \mathbf{R}_l)$. In fact, the ionic term in $V(\mathbf{K}_n)$ given by Eq. (8) greatly retards convergence of the sum except for the $\mathbf{K}_n$ dependence of E_{ij}. Even then the sum is extremely slow to converge for some i, j, and R_l. Since the electronic and exchange portions converge rapidly, an enhanced convergence rate of the ionic part would greatly facilitate the summation in Eq. (6).

An Ewald expansion [3, 11] allows cancellation of the ionic portion for large valves of $\mathbf{K}_n$. In this method a model potential is added to the crystal potential so that, in the limit of large $\mathbf{K}_n$, the Fourier transforms of the model potential and ionic potential cancel. Integrals of the model potential must be evaluated by some other method, so that this part may be subtracted off at the end:

$$V(\mathbf{r}) = -V_{\mathrm{m}}(\mathbf{r}) + \sum_n [V(\mathbf{K}_n) + V_{\mathrm{m}}(\mathbf{K}_n)]\, e^{i\mathbf{K}_n\cdot\mathbf{r}}. \tag{9}$$

Careful choice of V_{m} enhances the rate of convergence in reciprocal space; when balanced by a rapidly computed real-space expression, a decrease in total computational time is achieved. One suitable model potential is a Yukawa potential of the form

$$V_{\mathrm{m}}(\mathbf{r}) = \sum_l (Z_l e^2/|\,\mathbf{r} - \mathbf{R}_l\,|)\, e^{-\alpha|\mathbf{r}-\mathbf{R}_l|}, \tag{10}$$

where Z_l is the atomic number associated with site $\mathbf{R}_l$, and α is a parameter to be selected to enhance convergence. The Fourier transform is

$$V_{\mathrm{m}}(\mathbf{K}_n) = 4\pi Ze^2/\Omega(\alpha^2 + K_n{}^2), \tag{11}$$

where Ω is the volume of a unit cell.

Now, since the Fourier transform of the ionic potential is

$$V_{\mathrm{ion}}(\mathbf{K}_n) = -4\pi Ze^2/\Omega K_n{}^2, \tag{12}$$

the model potential asymptotically cancels the ionic portion for large K_n, as desired. For fixed K_n, the amount of cancellation between Eqs. (11) and (12) is determined by the smallness of α; however, too small a value will introduce convergence problems into Eq. (3). In order to take advantage of this cancellation of terms, it is necessary that the three-centered integrals of $V_{\mathrm{m}}(\mathbf{r})$ (now appearing in Eq. (3)) be evaluated accurately. Exact expressions for three-centered integrals of the model potential in Eq. (10) are given in the Appendix. To our knowledge, exact expressions for these multicentered integrals have not been previously applied, although one- and two-centered approximations have been applied for other model potentials [12].

4. RECIPROCAL-LATTICE SUMS FOR LiF

In this section formulas given in the Appendix are applied to compute LCAO integrals for crystalline LiF. These integrals have previously been obtained by Drost and Fry [15] in an energy band calculation by summing and using the extrapolation technique in Eq. (6). In order to compare with the Ewald results obtained here, the same wavefunctions listed in [15] are adopted, and the same potential is used.

The model potential parameters chosen for LiF are $Z = 3$ for Li ions, $Z = 9$ for F ions, and $\alpha = 2.0$ reciprocal atomic units for both ions. When a complete band structure calculation is made using this model crystalline potential for LiF, surprisingly good results are obtained for the lithium type energy bands. It appears that $\alpha = 2$ does not provide proper screening for the F ions, however, since the flourine bands were not accurately reproduced. On the other hand, this model potential is valid in performing the first-principles calculations using the Ewald procedure. Integral values obtained will be independent of the model potential parameters if all sums are converged, but the rate of convergence can be greatly influenced by the choice of parameters.

The criterion used here to select α is

$$(V_{\mathrm{ION}}(K) - V_{\mathrm{M}}(K))/V_{\mathrm{ION}}(K) < 10^{-6}$$

after 6000 reciprocal-lattice stars. It is found that the choice $\alpha = 2$ satisfies this condition and, in addition, simplifies some of the numerical work. A smaller value of α would speed up the reciprocal-lattice sums and slow down the direct-lattice sums. Ideally, it would be better to find a value which would minimize the total time. While reciprocal-lattice sums require evaluation of many exponential, sine, and cosine functions, direct-lattice sums entail exponentials and error functions, which are slower.

For $\alpha = 2$, the direct-lattice sums converge much more rapidly than the reciprocal-lattice sums, requiring at most 10–20 shells for a convergence criterion of 10^{-8} in the direct lattice. A value of α as much as an order of magnitude smaller might be feasible without making the direct-lattice sums too lengthy; the reciprocal-lattice sums would then converge well before 6000 stars. This option was not taken here because it is necessary to converge the electronic Fourier coefficients to about 1000 stars anyway.

The rate of convergence of different integral types depends most strongly upon the spatial extent of the wave functions used in constructing the LCAO, and the separation of the two centers in Eq. (7). The poorest convergence rate occurs for the central cell integrals ($R_l = 0$ in Eq. (7)). A comparison of the rate of convergence for lithium central cell integrals is presented in Table I. The fluorine central cell integrals converge more slowly. The convergence rate of all integrals improves rapidly for larger R_l.

The advantage of the Ewald method may be seen clearly by comparing the rate of convergence of V_{C} or V_{M} with $V_{\mathrm{C}} + V_{\mathrm{M}}$. While V_{C} has only two significant figures after 5000 stars, $V_{\mathrm{C}} + V_{\mathrm{M}}$ after 5000 stars may be used with an accurate value for V_{M} obtained from the direct-lattice expressions given in the Appendix to obtain a value of V_{C} accurate to at least five significant figures. In fact, the

TABLE I

Convergence of Fourier Series for Li–Li Central Cell Integrals[a]

No. RLV Stars	1s–1s			1s–2s			2s–2s		
	V_C	V_M	$V_C + V_M$	V_C	V_M	$V_C + V_M$	V_C	V_M	$V_C + V_M$
1000	−8.57595	8.56538	−0.010577	1.13375	−1.16441	−0.030664	−0.751842	0.816576	0.064734
5000	−8.62455	8.61381	−0.010740	1.14138	−1.17202	−0.030638	−0.753041	0.817771	0.064730
10,000	−8.63033	8.61958	−0.010748	1.14229	−1.17293	−0.030637	−0.753183	0.817913	0.064730
20,000	−8.63329	8.62254	−0.010750	1.14276	−1.17340	−0.030636	−0.753257	0.817987	0.064730
40,000	−8.63461	8.62386	−0.010751	1.14297	−1.17361	−0.030636	−0.753291	0.818021	0.064730
Ext.	−8.63609	8.62532	−0.010751	1.14326	−1.17380	−0.030636	−0.753326	0.818056	0.064730
Exact		8.62512			−1.17381			0.818054	

[a] V_C is the total coulomb integral, and V_M the model potential integral (in rydbergs). The row labeled Ext. contains extrapolated estimates. The last row contains exact values obtained from the direct-lattice expressions.

difference between the 5000 star value for $V_C + V_M$ and the extrapolated value may be attributed almost entirely to the electronic coulomb Fourier coefficients which have not been treated by the Ewald procedure. A corresponding treatment of the electronic contributions would reduce the number of required stars below 1000. For this purpose a slightly different model potential would be required.

In order to take advantage of rapid convergence of the Fourier expansion of $V_C + V_M$, it is necessary to have accurate values of integrals of $V_M(\mathbf{r})$ given in Eq. (10). Expressions for these integrals which are given in the Appendix were programmed for computer calculation with attention given to accuracy of the lattice sums and evaluation of error functions. The function $\Phi^{\pm}$ defined in the Appendix must be evaluated with special care for large values of the argument of the error function. Depending upon the sign of the argument, $\Phi^{\pm}$ must be evaluated using the complementary error function instead of the error function, or enormous errors will be introduced as a result of roundoff and multiplication by the exponential function. Convergence of the lattice sum in Eq. (10) was obtained to eight or more significant figures in every case.

Table II gives the direct-lattice sum for V_M and compares Ewald values of various integrals with values obtained by summing and extrapolating the Fourier series.

TABLE II

Ewald Converged Values for Li–Li and F–F Integrals[a]

$(2/a)R$.	Integral	Exp.	V_M	$V_C + V_M$	V_C (Ewald)	V_C (Fourier)	$V_C^{(2)}(E)$
000	Li–Li 1*s*–1*s*	0	8.62512	−0.01075	−8.63587	−8.63609	—
	1*s*–2*s*	0	−1.17381	−0.03064	1.14318	1.14326	—
	2*s*–2*s*	−1	8.18054	0.64730	−7.53325	−7.53326	—
000	F–F 1*s*–1*s*	2	1.15481	−0.00514	−1.15995	−1.15980	—
	1*s*–2*s*	1	2.11880	−.12540	+1.99340	2.00027	—
	2*s*–2*s*	0	9.40968	1.09920	−8.31048	−8.31063	—
310	Li–Li 1*s*–1*s*	−5	3.31189	−.2226	−3.53415	−3.53418	−3.44030
	1*s*–2*s*	−3	4.52443	−.30006	−4.82449	−4.82450	−4.61481
	2*s*–2*s*	−2	4.37521	.32336	−4.05185	−4.05184	0.27298
110	F–F 1*s*–1*s*	−5	1.59212	.14441	−1.44771	−1.44447	−1.44719
	1*s*–2*s*	−3	1.75007	.15935	−1.59072	−1.58718	−1.58960
	2*s*–2*s*	−3	2.42786	.47954	−1.94832	−1.94998	−1.69693

[a] R_l is the separation between the wavefunctions; a is the lattice constant. Exp. is the power of 10 by which integrals in each row must be multiplied. V_M is the direct-lattice integral of the model potential, $V_C + V_M$ and V_C are reciprocal-lattice sums for integrals of coulomb plus model potential and coulomb potential respectively. V_C (Ewald) and $V_C{}^2(E)$ are Ewald values for V_C using exact results for V_M and the two-center approximation for V_M, respectively.

These results are representative of the accuracy which may be achieved for different *ss* integrals; similar behavior occurs with *p* functions.

A number of observations may be made from the data presented in Table II. The central cell integrals were obtained by summing to 40,000 reciprocal-lattice stars, while the integrals evaluated for other separations contained sums out to 20,000 stars. In both cases the final value listed as V_C (Fourier) is an extrapolation of the sum. The reciprocal lattice sum for integrals of $V_C + V_M$ converged by 5000 stars to the number of significant figures quoted in the table, so that the value quoted for integrals of V_C (Ewald) would remain unchanged upon summing an additional 35000 stars. The data in Table I may be used to demonstrate that a value of the integral accurate to five significant figures would be achieved using information obtained after only 1000 stars. This is possible, in part, because, not only is the Fourier transform of $V_C + V_M$ small for large K_n, but the sum of integrals of the Fourier series of $V_C + V_M$ is also a small quantity. Thus a calculation to three significant figures for $V_C + V_M$, when combined with a value of V_M accurate to five significant figures, provides five significant figures for V_C. Depending on the model potential parameters, this may not always be the case.

Table II indicates good agreement between the Fourier series method and the Ewald method for integrals involving functions which are long-ranged; but integrals with one short-ranged orbital differ. The conclusion obtained is that, while extrapolation of the Fourier series can yield three or four significant figures, the time required is more than 100 times as long as the Ewald procedure to provide a comparable accuracy.

The last column in Table II gives the value of the coulomb integral obtained by using a two-center approximation to simplify evaluation of the direct-lattice sums for integrals of V_M. This approximation has often been made to simplify first-principles calculations and was made in a previous application of the Ewald procedure [12]. For the model potential and LCAO functions employed here, this approximation is seen to introduce significant errors into the coulomb integral. For nearer Li–Li neighbors the errors were found to be as large as 0.5 rydbergs for the 2*s*–2*s* integrals. For a good choice of V_M the three-centered expressions may be summed rapidly, so the two-center approximation is neither appropriate nor necessary.

5. CONCLUSION

A model potential has been found which may be used effectively in the Ewald procedure to obtain reciprocal-lattice sums. It is characterized by a Fourier transform which is finite at $K = 0$, and approaches the Fourier transform of a point ion for large K. Integrals of the model potential, including all multicentered terms, may be evaluated analytically if Gaussian LCAO basis functions are employed. By appropriate choice of parameters in the model potential it is possible to obtain rapid convergence in both reciprocal-lattice and direct-lattice sums. For a desired degree of accuracy, this Ewald procedure reduces the total computational time by as much as two orders of magnitude.

APPENDIX

In the Ewald procedure it is necessary to evaluate integrals of the model potential of the type

$$I = \int \exp(-\alpha_1 \mid \mathbf{r} - \mathbf{A} \mid^2)(\exp(-\alpha \mid \mathbf{r} - \mathbf{C} \mid)/\mid \mathbf{r} - \mathbf{C} \mid) \exp(-\alpha_2 \mid \mathbf{r} - \mathbf{B} \mid^2)\, d\mathbf{r} \quad \text{(A1)}$$

for s-type Gaussian orbitals centered on sites **A** and **B**, and the model potential on site **C**. Similar integrals for p and d symmetries may be obtained from the s integrals by differentiation with respect to an appropriate parameter once an expression for the ss integral is obtained. The ss three-center integral may be computed exactly by using properties of the Gaussian orbitals to reduce it to a two-center integral. The two-center integral is then evaluated in spheroidal coordinates for any model potential which may be expressed as a product of a Gaussian or exponential function times a rational function of $\mid \mathbf{r} \mid$. Expressions for ss, sp, and pp integrals are given here. Details are given in [16].

The center of the product of two s type Gaussian orbitals, one at **A**, the other at B, is $\mathbf{D} = (\alpha_1 \mathbf{A} + \alpha_2 \mathbf{B})/(\alpha_1 + \alpha_2)$. Define $R = \mid \mathbf{D} - \mathbf{C} \mid$, $R_{AB} = \mid \mathbf{B} - \mathbf{A} \mid$. Then including the proper normalization factor for the Gaussian orbitals and defining

$$\begin{aligned}
C_{ss} &= Z(2/\pi)^{3/2}\,(\alpha_1\alpha_2)^{3/4} \exp(-\alpha_1\alpha_2 R_{AB}^2/\beta),\\
C_{sp} &= Z(2\alpha_1/\pi)^{3/4}\,(128\alpha_2{}^5/\pi^3)^{1/4} \exp(-\alpha_1\alpha_2 R_{AB}^2/\beta),\\
C_{pp} &= Z(128/\pi^3)^{1/2}\,(\alpha_1\alpha_2)^{5/4} \exp(-\alpha_1\alpha_2 R_{AB}^2/\beta),\\
\beta &= \alpha_1 + \alpha_2\,, \qquad \lambda_i = B_i - A_i\,, \qquad \eta_i = D_i - C_i\,, \qquad \text{(A2)}\\
N &= (\pi^{3/2}/\beta^{3/2}) \exp(\alpha^2/4\beta),\\
M &= (2\pi/\beta^2) \exp(-\beta R^2),\\
\Phi^{\pm} &= \exp(\pm\alpha R)[\operatorname{erf}(\beta^{1/2} R \pm (\alpha/2\beta^{1/2}) \mp 1],
\end{aligned}$$

the ss three-center integral for the model potential is

$$I_{ss} = C_{ss}(N/R)[\Phi^+ + \Phi^-]. \qquad \text{(A3)}$$

The *sp* integrals are, with *s* on **A**, *p* on **B**,

$$I_{sp_i} = C_{sp}\{(M/R^2)\,\eta_i - (N/2\beta R^3)[(\Phi^+ + \Phi^-)(2\alpha_1 R^2\lambda_i + \eta_i) - (\Phi^+ - \Phi^-)\,\alpha R\eta_i]\}. \tag{A4}$$

Define

$$\begin{aligned} x^{\pm} = \Phi^{\pm}[&4\alpha_1\alpha_2 R^4\lambda_i\lambda_j - (3 \mp 3\alpha R + \alpha^2 R^2)\,\eta_i\eta_j - (2\alpha_1 R^2 \mp 2\alpha\alpha_1 R^3)\,\lambda_j\eta_i \\ &+ (2\alpha_2 R^2 \mp 2\alpha\alpha_2 R^3)\,\lambda_i\eta_j + (R^2 \mp \alpha R^3 - 2\beta R^4)\,\delta_{ij}], \end{aligned} \tag{A5}$$

where δ_{ij} is the Kronecker delta. The *pp* three-center result is

$$\begin{aligned} I_{p_ip_j} = -\,C_{pp}\{&(M/\beta R^2)[(\beta + (3/2R^2))\,\eta_i\eta_j + \alpha_1\lambda_j\eta_i - \alpha_2\lambda_i\eta_j - \tfrac{1}{2}\delta_{ij}] \\ &+ (N/4\beta^2 R^5)[x^+ + x^-]\}. \end{aligned} \tag{A6}$$

If the sites **A**, **B**, and **C** are such that the integral reduces to one or two centers, it is necessary to obtain integrals expressions as a limit of the three-center expressions given above. The formulas are simple, but will not be quoted here.

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