THE PROBLEM OF NON-ORTHOGONALITY OF ATOMIC ORBITALS IN THE APPLICATION OF THE HEITLER-LONDON METHOD TO CRYSTALS

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The problem of the non-orthogonality of the atomic orbitals in the Heitler-London method is considered for the case in which the state of the system is described by a linear combination of Slater determinants which differ both in their spin and their orbital configurations. An approach is developed on the basis of taking into account completely the most important overlap integrals. Sufficient conditions for the applicability of this approach are formulated.

INTRODUCTION

ALREADY in the 1930's a number of authors[1-3] have drawn attention to the difficulties connected with the application of the Heitler-London method to many-electron problems because of the lack of orthogonality of the one-electron wave functions. It was shown in the simple example of a linear chain of hydrogen-like atoms that if the total number N of electrons is large, and the non-orthogonality of the one-electron wave functions is allowed for, the expression for the energy of the system appears as a ratio of two polynomials in N in which the coefficients of the various powers of N are the overlap integrals of one-electron wave functions. If N is large then the usual approach in which the overlap integrals are completely neglected may have a very large error. Moreover this error may increase indefinitely with increasing N. This difficulty in the theory is called "the non-orthogonality disaster." The problem was analyzed in the papers of Van Vleck[3], Carr[4], and Mizuno and Izuyama[5].

In these papers the state of the system was described by a single Slater determinant. This limitation, which simplifies the problem considerably, is a very serious restriction, since only very few problems can be satisfactorily treated by this choice of the many electron wave function. In recent years the work of Arai[6,7] and Mullin[8] has dealt with the case in which the state is described by a linear combination of Slater determinants. Here the separate determinants differed only in their spin configurations while the orbital configuration remained the same. In addition it was assumed that the orbital configuration corresponded to the ground state of the system, so that the orbital functions did not include excited states of atoms. In the present paper we consider the more general case, in which the system is described by a linear combination of Slater determinants which differ both in their spin and in their orbital configurations. An approach is developed which already in zero-order approximation allows explicitly for the most important overlap integrals which cannot be regarded as small. Conditions for the applicability of this approach are formulated. These conditions are generalizations of the relations found by Mizuno and Izuyama[5].

2. GENERALIZED HEITLER-LONDON METHOD

The generalized Heitler-London method for the solution of quantum mechanical problems requires first of all the choice of a system of zero-order wave functions

$$\Phi_i = \Phi_i(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \quad i = 1, \ldots, M), \tag{1}$$

which depend on the coordinates and spins of all electrons in the crystal. Each of these M functions (1) represents a separate Slater determinant

$$\Phi_i = c_i^{-1/2} A [v_1(\mathbf{x}_1) v_2(\mathbf{x}_2) \ldots v_k(\mathbf{x}_k) v_{k+1}(\mathbf{x}_{k+1}) \ldots v_N(\mathbf{x}_N)], \tag{2}$$

where A is the antisymmetrizing operator and c_i is a normalization constant. The one-electron functions $v_1(\mathbf{x}), \ldots, v_N(\mathbf{x})$ depend both on the space coordinates $\mathbf{r}$ and on the spin coordinate σ of the electrons ($\mathbf{x} = \mathbf{r}, \sigma$). In general these functions will not be mutually orthogonal.

After relabelling rows and columns, any two Slater determinants from the set (1) can be expressed in the form

$$\Phi_\alpha = c_\alpha^{-1/2} A[v_1(\mathbf{x}_1)\ldots v_k(\mathbf{x}_k) v_{k+1}(\mathbf{x}_{k+1})\ldots v_N(\mathbf{x}_N)], \quad (3)$$

$$\Phi_\beta = c_\beta^{-1/2} A[u_1(\mathbf{x}_1)\ldots u_k(\mathbf{x}_k) v_{k+1}(\mathbf{x}_{k+1})\ldots v_N(\mathbf{x}_N)]. \quad (4)$$

The choice of the two sets of functions $v_1, \ldots, v_k$ and $u_1, \ldots, u_k$ for any pair of Slater determinants Φ_α and Φ_β is done in such a way that the factors v_j $(j = k + 1, \ldots, N)$ do not contain excited atomic wave functions. The number k of different functions in (3) and (4) is usually small $(k \ll N)$, since in most practical cases the transition from one state Φ_α of the crystal to another Φ_β involves only changes of state for a small number of electrons. The limiting case of $k = N$ has been considered by Löwdin[9]. However, the problem here becomes so complicated that it is not possible to get beyond very general formulae.

As a result of the non-orthogonality of the one-electron wave functions the set of functions (1) are also not orthogonal. In order to avoid difficulties which might arise from this we introduce in place of (1) an orthogonalized system of wave functions of zero order[10,11]:

$$\Psi_i = \sum_{j=1}^{M} \Phi_j [(1+Q)^{-1/2}]_{ji}, \quad i = 1, \ldots, M, \quad (5)$$

where Q is the matrix of the non-orthogonality integrals of the many-electron wave functions Φ_j with the elements

$$Q_{ji} = \int \Phi_j^* \Phi_i \, d\tau - \delta_{ij}. \quad (6)$$

Here and later the symbol $\int d\tau$ denotes integration and summation over all electron variables.

The wave function of an arbitrary state of the crystal can be written in the form

$$\Psi = \sum_{i=1}^{M} a_i \Psi_i. \quad (7)$$

The function Ψ will be normalized to unity if the coefficients a_i obey the condition $\sum_i |a_i|^2 = 1$. The rest amounts to the determination of the coefficients a_i as the solution of a suitable secular equation, and subsequently to the calculation of the averages over the function Ψ of various physical quantities. Thus in essence the problem consists of the calculation of the matrix elements of various operators, which are symmetric in the electron coordinates, between the orthonormalized functions Ψ_i.

Consider the matrix element

$$\int \Psi_i^* \Omega \Psi_j \, d\tau, \quad (8)$$

where the operator Ω is symmetric in the electron coordinates. In all cases of practical interest the operator Ω is a sum of one or two electron operators, i.e.,

$$\Omega = \begin{cases} \Omega_{\mathrm{I}} = \sum\limits_{l=1}^{N} \Omega_l \\ \Omega_{\mathrm{II}} = \sum\limits_{k<l=1}^{N} \Omega_{kl}. \end{cases} \quad (9)$$

By substituting (5) in (8) we find

$$\int \Psi_i^* \Omega \Psi_j \, d\tau = \sum_{\alpha,\beta=1}^{M} [(1+Q)^{-1/2}]_{i\alpha} \int \Phi_\alpha^* \Omega \Phi_\beta \, d\tau \, [(1+Q)^{-1/2}]_{\beta j} \quad (10)$$

or in matrix form

$$A = (1+Q)^{-1/2} B (1+Q)^{-1/2}, \quad (11)$$

where A denotes the matrix with the elements $\int \Psi_i^* \Omega \Psi_j \, d\tau$ obtained from the orthonormalized functions (5), and B a matrix with the elements $\int \Phi_\alpha^* \Omega \Phi_\beta d\tau$ obtained from the original zero-order wave functions (1).

2. CALCULATION OF THE MATRIX ELEMENTS OF B

By definition the elements of the matrix B have the form

$$B_{\beta\alpha} = \int \Phi_\beta^* \Omega \Psi_\alpha \, d\tau, \quad (12)$$

where Φ_β and Φ_α are determinants defined by (3) and (4). To evaluate (12) we may use a combined orthogonalization method[12,13] the idea of which is based on a separation of all possible overlap integrals into two groups: (a) the set of integrals $\bar{S}$ which may not be assumed to be small since they may contain excited atomic functions, and (b) the numerous small overlap integrals S which do not involve excited wave functions. The evaluation of the matrix element $B_{\beta\alpha}(\mathrm{I}) = \int \Phi_\beta^* \Omega_{\mathrm{I}} \Phi_\alpha d\tau$ gives[13]

$$\begin{aligned} B_{\beta\alpha}(\mathrm{I}) = D_{vv}^{-1/2} D_{uu}^{-1/2} \Bigg\{ \sum_{\mu,\nu=1}^{k} (-1)^{\mu+\nu} D_{uv}(\mu|\nu) \\ \times \Bigg[\int u_\mu^*(1) \Omega_1 v_\nu(1) \, d\mathbf{x}_1 \\ - \sum_{i,j=k+1}^{N} \int u_\mu^*(1) \Omega_1 v_i(1) \, d\mathbf{x}_1 T_{ij} \bar{S}_{j\nu}^{(v)} \\ - \sum_{i,j=k+1}^{N} \bar{S}_{\mu i}^{(u)} T_{ij} \int v_j^*(1) \Omega_1 v_\nu(1) \, d\mathbf{x}_1 \\ + \sum_{i,i'\, j,j'} \bar{S}_{\mu i}^{(u)} T_{ij} \int v_j^*(1) \Omega_1 v_{j'}(1) \, d\mathbf{x}_1 T_{j'i'} \bar{S}_{i'\nu}^{(v)} \Bigg] \end{aligned}$$

$$+D_{uv}\sum_{i,j=k+1}^{N} T_{ij}\int v_i^*(1)\,\Omega_1 v_j(1)\,d\mathbf{x}_1\Big\}, \tag{13}$$

where

$$D_{vv}=\det\{\bar d_{vv}(\mu\nu)\},$$
$$D_{uu}=\det\{\bar d_{uu}(\mu\nu)\},$$
$$D_{uv}=\det\{\bar d_{uv}(\mu\nu)\}$$

are determinants of order k and $D_{uv}(\mu/\nu)$ is a minor of first order of the determinant D_{uv} with respect to the element μ, ν. The elements of the determinants D_{vv}, D_{uu}, D_{uv} are given by the expressions

$$\bar d_{vv}(\mu\nu)=(v_\mu, v_\nu)-\sum_{i,j=k+1}^{N}\bar S_{\mu i}{}^{(v)}T_{ij}\bar S_{j\nu}{}^{(v)},$$
$$\bar d_{uu}(\mu\nu)=(u_\mu, u_\nu)-\sum_{i,j=k+1}^{N}\bar S_{\mu i}{}^{(u)}T_{ij}\bar S_{j\nu}{}^{(u)},$$
$$\bar d_{uv}(\mu\nu)=(u_\mu, v_\nu)-\sum_{i,j=k+1}^{N}\bar S_{\mu i}{}^{(u)}T_{ij}\bar S_{j\nu}{}^{(v)}, \tag{14}$$

The symbols $\bar S_{\mu i}^{(u)}$ and $\bar S_{j\nu}^{(v)}$ denote overlap integrals between the functions u_μ, v_μ ($\mu = 1, \ldots, k$) on the one hand, and the functions v_i ($1 = k + 1, \ldots, N$) on the other:

$$\bar S_{\mu i}{}^{(u)}=(u_\mu, v_i),\qquad \bar S_{j\nu}{}^{(v)}=(v_j, v_\nu). \tag{15}$$

The matrix T has the form

$$T_{ij}=(1+S)_{ij}^{-1}=\delta_{ij}-S_{ij}+\sum_{l=k+1}^{N}S_{il}S_{lj}-\ldots, \tag{16}$$

where $S_{ij} = (v_i, v_j) - \delta_{ij}$ is the overlap integral of the function v_i ($i = k + 1, \ldots, N$) with itself.

A similar formula can be obtained for the matrix element $B_{\beta\alpha}(\mathrm{II}) = \int\Phi_\beta^*\Omega_{\mathrm{II}}\Phi_\alpha d\tau$. However, it is so lengthy that it is more sensible to write it in a different form:

$$B_{\beta\alpha}(\mathrm{II})=\sum_{\mu<\nu}D_{uv}(\mu\nu|\mu\nu)\{[\mu\nu|\Omega_{12}|\mu\nu]-[\mu\nu|\Omega_{12}|\nu\mu]\}$$
$$+\sum_{\mu=1}^{k}\sum_{j=k+1}^{N}D_{uv}(\mu|\mu)\{[\mu j|\Omega_{12}|\mu j]-[\mu j|\Omega_{12}|j\mu]\}$$
$$+D_{uv}\sum_{i,\,j=k+1}^{N}\frac{1}{2}\{[ij|\Omega_{12}|ij]-[ij|\Omega_{12}|ji]\}, \tag{17}$$

where $D_{uv}(\mu\nu\,|\,\mu\nu)$ is a second order minor of the determinant D_{uv} with respect to the elements $\mu\mu$, $\nu\nu$. In addition we have used the following abbreviations:

$$[\mu\nu|\Omega_{12}|\mu\nu]=\int\bar u_\mu{}^*(1)\,\bar u_\nu{}^*(2)\,\Omega_{12}\bar v_\mu(1)\,\bar v_\nu(2)\,d\mathbf{x}_1\,d\mathbf{x}_2,$$
$$[\mu j|\Omega_{12}|\mu j]=\int\bar u_\mu{}^*(1)\,\varphi_j(2)\,\Omega_{12}\bar v_\mu(1)\,\varphi_j(2)\,d\mathbf{x}_1\,d\mathbf{x}_2,$$
$$[ij|\Omega_{12}|ij]=\int\varphi_i{}^*(1)\,\varphi_j{}^*(2)\,\Omega_{12}\varphi_i(1)\,\varphi_j(2)\,d\mathbf{x}_1\,d\mathbf{x}_2,$$

where the functions $\bar u_\mu$, $\bar v_\mu$, φ_j are defined by

$$\bar u_\mu=u_\mu-\sum_{j=k+1}^{N}\varphi_j(\varphi_j, u_\mu),$$
$$\bar v_\mu=v_\mu-\sum_{j=k+1}^{N}\varphi_j(\varphi_j, v_\mu),$$

$$v_j=\sum_{i=k+1}^{N}v_i(1+S)_{ij}^{-1/2}. \tag{18}$$

On inserting (18) in (17) one obtains an expression similar to (13) which contains the overlap integrals $\bar S^{(u)}$, $\bar S^{(v)}$ and the matrix elements of T (16). Equations (13), (17) and (18) give exact expressions for the matrix elements $B_{\beta\alpha}(\mathrm{I})$, $B_{\beta\alpha}(\mathrm{II})$, allowing for all overlap integrals: in addition to the particularly important quantities $\bar S^{(u)}$ and $\bar S^{(v)}$, which contain excited atomic wave functions a large number of small overlap integrals are allowed for in the matrix T.

3. ZERO-ORDER APPROXIMATION AND "THE NON-ORTHOGONALITY DISASTER"

In the preceding section it was shown that, allowing for the non-orthogonality of the one-electron wave functions in the Heitler-London method, the matrix elements of the Hamiltonian and other operators contain a large number of different overlap integrals. Therefore the error in the usual method in which the non-orthogonality of the one-electron wave functions is completely neglected may be considerable. This "non-orthogonality disaster" is made worse by the fact that these overlap integrals include some which manifestly are not small, since they contain excited atomic wave functions which are strongly de-localized. We shall deal with this by renormalization of the zero approximation. A similar approach was used by Mizuno and Izuyama in their theory of bound electron pairs[5] and also by Gold[14] in the theory of impurity centers. Basically this method amounts to neglecting in the zeroth approximation the large number of small overlap integrals which do not contain excited atomic states. Explicitly, one assumes in zero-order approximation

$$T_{ij}=\delta_{ij}. \tag{19}$$

By using the results of Mizuno and Izuyama[5] one can show that, provided the overlap integral S_{ij} obeys the condition

$$\sum_{l=k+1}^{N}|S_{lj}|\leqslant 1/2 \tag{20}$$

then for any $j = k + 1, \ldots, N$ the matrix elements of T satisfy

$$\left(1+\sum_{l=k+1}^{N}|S_{li}|\right)^{-1} \leqslant T_{ii} \leqslant \left(1-\sum_{l=k+1}^{N}|S_{li}|\right)^{-1}, \quad (21)$$

$$|T_{ij}| \leqslant \sum_{l=k+1}^{N}|S_{lj}| \Big/ \left[1-\sum_{l=k+1}^{N}|S_{li}|\right]\left[1-\sum_{l=k+1}^{N}|S_{lj}|\right]. \quad (22)$$

It follows that the exact values of the matrix elements of T do not differ much from the approximate values $T_{ij} = \delta_{ij}$ if the expression $\sum_{i=k+1}|S_{ij}|$ is sufficiently small compared to 1/2.

If the non-orthogonality integrals (6) of the many electron functions Φ_i ($i = 1, \ldots, M$) are small enough, the matrix elements of $(1 + Q)^{-1/2}$ can be expanded

$$(1+Q)_{ji}^{-1/2} = \left(1-\frac{1}{2}Q+\frac{3}{8}Q^2-\ldots\right)_{ji}$$

$$= \delta_{ji} - \frac{1}{2}Q_{ji} + \frac{3}{8}\sum_{\alpha=1}^{M}Q_{j\alpha}Q_{\alpha i} - \ldots \quad (23)$$

The question of the convergence of the series (23) is of great importance for the discussion of the "non-orthogonality disaster." Löwdin[10] has shown that the matrix series (23) will converge if

$$\sum_{\beta=1}^{M}|Q_{\beta\alpha}| = q < 1, \quad (24)$$

for any $\alpha = 1, \ldots, M$. It converges more rapidly the smaller is Q compared to unity. By using the definition (6) we can express this condition in the form

$$\sum_{\beta\neq\alpha}\left|\int \Phi_\beta^* \Phi_\alpha \, d\tau\right| < 1. \quad (25)$$

We evaluate the integrals occurring here by means of the combined orthogonalization method and find[13]:

$$\int \Phi_\beta^* \Phi_\alpha \, d\tau = D_{vv}^{-1/2} D_{uu}^{-1/2} D_{uv}. \quad (26)$$

It follows that the series for $(1 + Q)^{-1/2}$ will converge if

$$\sum_u{}' |D_{uv}(D_{uu}D_{vv})^{-1/2}| = q < 1; \quad (27)$$

here the inequality (27) must hold for any of the M sets of functions $v_1, \ldots, v_k$, which occur in (1). The summation here extends over the $M - 1$ sets of functions $u_1, \ldots, u_k$ which differ from $v_1, \ldots, v_k$. The elements of the determinants D_{vv}, D_{uu}, D_{uv} (14) will contain overlap integrals without excited atomic states but may include in addition overlap integrals of two other types: $\overline{S}$, which contain only one excited function, and $\overline{\overline{S}}$, containing two excited functions. Hence the inequalities (20) and (27) are conditions which can be applied directly to the magnitude of the overlap integrals S, $\overline{S}$, $\overline{\overline{S}}$. These can be regarded as generalizations of the conditions of Mizuno and Izuyama[5] to the case in which the state of the system is described by a linear combination of determinants which differ in their spin as well as in their orbital configurations.

If the condition (27) is satisfied the matrix A (11) can be expanded in powers of Q:

$$A = B - {}^1/_2(QB + BQ) + \ldots . \quad (28)$$

The error arising from neglecting higher powers of Q will be smaller the smaller (27) compared to unity.

4. DISCUSSION OF THE PROBLEM FOR THE EXAMPLE OF NOBLE GAS CRYSTALS

For a more detailed analysis of conditions (20) and (27) consider a simple cubic Bravais lattice of N atoms with complete electron shells. Then the state of each electron in the system can be described by an atomic wave function ψ_{Ii} which is localized near some lattice point I, and where i is the set of quantum numbers for the electron in the atom. According to (11) we introduce a system of wave functions of zero approximation corresponding to a localized excitation when any one of the atoms is in the excited state with the configuration $np^5n's$:

$$\Phi_{J\lambda} = A\overline{\psi}_{J\varkappa}(\mathbf{x}_{J\varkappa}) \prod_{Ll\neq Jj} \psi_{Ll}(\mathbf{x}_{Ll}), \quad (29)$$

where $\overline{\psi}_{J\kappa}$ is the wave function for an excited electron. Here it has been assumed that the change in the wave functions of the electrons in the p shell can be neglected, so that the functions ψ_{Ll} ($Ll \neq Jj$) are the same as in the ground state. There exist therefore 12N separate Slater determinants which differ from each other by the functions occurring in two columns.

Indeed the functions $\Phi_{J\lambda}$ and $\Phi_{I\lambda'}$ can be written in the form (3) and (4) if one sets

$$v_1 = \psi_{Ii}, \; v_2 = \overline{\psi}_{J\varkappa}; \quad u_1 = \overline{\psi}_{I\varkappa}, \; u_2 = \psi_{Jj}. \quad (30)$$

The quantities D_{vv}, D_{uu}, D_{uv} are in this case determinants of the second order. We shall from now on take into account only the overlap of wave functions of the outer np shells of the atoms in the crystal. Since in addition, the overlap integrals decrease rapidly with increasing R (R is the distance between the centers on which the atomic functions are localized) we may limit the consideration to three relative positions $R_1 = a$, $R_2 = a\sqrt{2}$, $R_3 = a\sqrt{3}$ where a is the lattice constant. With these assumptions the condition (20) takes the form

$$q_1 = 6|S_{R_1}(np\sigma, np\sigma)| + 12|S_{R_2}(np\sigma, np\sigma)| + 8|S_{R_3}(np\sigma, np\sigma)| \leqslant {}^1/_2, \quad q_2 = 6|S_{R_1}(np\pi, np\pi)| + 12|S_{R_2}(np\pi, np\pi)| + 8|S_{R_3}(np\pi, np\pi)| \leqslant {}^1/_2. \tag{31}$$

Here we have used the standard notation for atomic p orbitals in a diatomic configuration[15]. The overlap integrals appearing in (31) have been calculated for n = 3 (argon) by Knox[16]. We then find for q_1 and q_2 with n = 3: $q_1 = 0.1897$, $q_2 = 0.0292$. For solid argon the condition (20) is therefore satisfied.

The general matrix elements of T reduce in the case in question to five basic types

$$T_{11} = T_{L3p\sigma,\, L3p\sigma}; \quad T_{22} = T_{L3p\pi,\, L3p\pi}; \quad T_{12} = T_{L3p\sigma,\, L3p\pi}, \quad T_{K3p\sigma,\, L3p\pi}; \quad T_{KL}(11) = T_{K3p\sigma,\, L3p\sigma}, \quad T_{KL}(22) = T_{K3p\pi,\, L3p\pi}.$$

Using the relations (21) and (22) we obtain

$$\frac{1}{1+q_1} \leqslant T_{11} \leqslant \frac{1}{1-q_1}, \quad \frac{1}{1+q_2} \leqslant T_{22} \leqslant \frac{1}{1-q_2}, \quad |T_{12}| \leqslant \frac{q_2}{(1-q_1)(1-q_2)};$$
$$|T_{KL}(11)| \leqslant q_1/(1-q_1)^2, \quad |T_{KL}(22)| \leqslant q_2/(1-q_2)^2. \tag{32}$$

If we insert here the values $q_1 \approx 0.2$ and $q_2 \approx 0.03$ we find that the greatest error arising from the replacement of the diagonal matrix elements of T by the approximation $T_{ii} = 1$ is for solid argon below 20%. In fact the error is less because Eqs. (13) and (17) contain terms independent of T, and this reduces the relative error. For an estimate of the error arising from the omission of the off-diagonal matrix elements of T one requires to know the order of magnitude of the terms without T in (13) and (17).

By evaluating the determinants D_{vv}, D_{uu}, D_{uv} to second order in the overlap integrals and retaining only terms involving excited atomic wave functions one brings the condition (27) to the form

$$q = \Big[1 - \sum_{Kk \neq Jj} |(\bar{\psi}_{J\varkappa}, \psi_{Kk})|^2\Big]^{-1/2} \sum_{Ii \neq Jj} |(\bar{\psi}_{J\varkappa}, \bar{\psi}_{I\varkappa})| |(\psi_{Jj}, \psi_{Ii})| \times \Big[1 - \sum_{Kk \neq Ii} |(\bar{\psi}_{I\varkappa}, \psi_{Kk})|^2\Big]^{-1/2} < 1. \tag{33}$$

We introduce the two parameters

$$q_0 = \sum_{Kk} |\bar{\psi}_{J\varkappa}, \psi_{Kk})|^2 = 6|S_{R_1}(n's, np\sigma)|^2 + 12|S_{R_2}(n's, np\sigma)|^2 + 8|S_{R_3}(n's, np\sigma)|^2,$$
$$q_3 = 6|S_{R_1}(n's, n's)||S_{R_1}(np\sigma, np\sigma)| + 12|S_{R_2}(n's, n's)| \times |S_{R_2}(np\sigma, np\sigma)| + 8|S_{R_3}(n's, n's)||S_{R_3}(np\sigma, np\sigma)|. \tag{34}$$

We may then replace the condition (33) by

$$q = q_3/(1 - q_0) < 1. \tag{35}$$

We use the actual values of the overlap integrals for solid argon[16] and find $q_3 = 0.09816$, $q_0 = 0.05985$. This makes q about 0.1. It is therefore clear that the inequality (27) is satisfied for solid argon and that the matrix series (23), for $(1 + Q)^{-1/2}$ converges sufficiently rapidly.

The results of this section lead to the conclusion that in the case of crystalline noble gases the approach based on equations (13), (17), and (28) with $T_{ij} = \delta_{ij}$ is applicable with a good accuracy. In this procedure the error remains small, however large the number of atoms in the crystal.

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