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Studies on Localized Orbitals*

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Wannier functions for free electrons in one dimension are discussed in some detail. The effects of the choice of lattice points and unit cell size are discussed, and details of the symmetry properties of the one-dimensional nearly-free-electron wave functions are given. The general relation between symmetry in the local site and three-dimensional space group symmetry is given. The possibilities for localized orbital treatments of metals and perturbed lattices are considered, and the electronic structure of CdSb is examined in terms of localized orbitals. The term *site orbital* is proposed to include the special cases of Wannier functions and Lennard-Jones equivalent orbitals.

INTRODUCTION

A NUMBER of different kinds of localized orbitals have been discussed in recent years. Wannier functions have been given a central position in Slater's[1] work; they are defined by

$$a(\mathbf{q}-\mathbf{Q}_n)=N^{-\frac{1}{2}}\sum_{\mathbf{p}_0} u_{\mathbf{p}_0}(\mathbf{q})\exp(-i\mathbf{p}_0\cdot\mathbf{Q}_n/\hbar), \qquad (1)$$

in which $\mathbf{p}_0$ runs over *all* the crystal momenta of a band, not just those for which the corresponding functions $u_{\mathbf{p}_0}$ are occupied. There are some ambiguities in this definition for multidimensional cases, with respect particularly to the question of which functions are to be included in a band.

Lennard-Jones' school[2] has placed special emphasis on the equivalent orbital (EO). The EO work has dealt mostly with molecules, but there has been an application[3] to crystals of the diamond structure. EO are defined as a set of orbitals spanning the same function space as some set of filled molecular orbitals or crystal orbitals, but having the property that their constant value surfaces are of identical shape, differing only in location and/or orientation. An antisymmetrized determinant of EO can be shown to be the same function of electron coordinates and spins as the antisymmetrized determinant of the molecular or crystal orbitals from which the EO are formed. As Lennard-Jones has shown, this property arises from the degrees of freedom possessed by the solutions of a multielectron Schrödinger equation according to the Hartree-Fock method.

It proves convenient to make use of a kind of orbital for which we shall introduce the designation "site orbital" (SO). These SO are like EO except that they need not be limited to being linear combinations of filled orbitals; EO are thus special cases of SO. SO in general do not have the EO property mentioned at the end of the last paragraph. The number of SO in a set is the product of the number of equivalent sites of a kind in the molecule or crystal by the degeneracy of the site orbital in the site symmetry.

The great advantage of the EO approach is that certain features of the EO theory correspond to the chemical ideas of bond, resonance, and atomic orbitals left unaffected by bonding. Discussing molecular orbital theory in EO terms enables contact to be made with these chemical ideas, thus clarifying the connection between theory and experiment. Application of the same kind of idea in crystals has not progressed as far.

WANNIER FUNCTIONS FOR FREE ELECTRONS

It seems worth while to examine the Wannier functions for free electrons in more detail than previous authors as a prelimary to the discussion of symmetry properties of localized orbitals. We begin by setting up Wannier functions for the bands in a one-dimensional, almost-free-electron situation. Our one-dimensional crystal has the unit cell length α, and is N unit cells long, with a total length L given by $N\alpha$. Except for functions with energies in the immediate neighborhood of the band gap, the eigenfunctions are

$$L^{-\frac{1}{2}}\exp(ip\cdot q/\hbar). \qquad (2)$$

As the perturbation is decreased and the potential becomes more nearly that for completely free electrons, the neighborhoods of the band gaps are contracted, the gaps themselves decrease, and the functions at the band gaps become, for the nth band, as is well known,

$$\left(\frac{2}{L}\right)^{\frac{1}{2}}\begin{Bmatrix}\cos\\ \sin\end{Bmatrix}\begin{Bmatrix}n\\ n-1\end{Bmatrix}\frac{\pi}{\alpha}q. \qquad (3)$$

In a perfectly free-electron case, there are no band gaps, and any length at all might be chosen for α. The assignment of functions to bands depends on the choice of α; we will take advantage of this when we discuss the effect of choosing unit cell lengths which are multiples of the primitive length.

The Wannier function for the lth band is given by

$$a^l(q-Q_n)=N^{-\frac{1}{2}}\sum_{p_0} u_{p_0}{}^l(q)\exp(-ip_0\cdot Q_n/\hbar). \qquad (4)$$

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* Supported in part by the Signal Corps.

[1] J. C. Slater, Phys. Rev. 76, 1592 (1949); 87, 807 (1952), and references therein.

[2] J. E. Lennard-Jones, Proc. Roy. Soc. (London) A198, 1 (1949) and many later papers.

[3] G. G. Hall, Phil. Mag. 43, 338 (1952).

Evidently the form of $a(q-Q_n)$ depends on the choice of phases for the eigenfunctions. The choice made in expressions (2) is only one of many possibilities; in a later section we consider the implications of this, meanwhile keeping to the phases of Eq. (2). Substitution in Eq. (4) gives on this basis

$$a^l(q-Q_n)=(NL)^{-\frac{1}{2}}\sum_{p=(l-1)h/2\alpha}^{lh/2\alpha}\{\exp[ip(q-Q_n)/\hbar] +\exp[-ip(q-Q_n)/\hbar]\}. \quad (5)$$

The p's in the summation are to be chosen by the periodic boundary condition

$$p=(m/N)(h/\alpha), \quad (6)$$

with m integral. It is to be noted that Eq. (5) is really inconsistent with Eq. (4) in terms of order $N^{-\frac{1}{2}}$; the band edge functions are really given by Eq. (3), and the band edge functions used in (4) are

$$L^{-\frac{1}{2}}\cos\left\{\begin{matrix} l-1 \\ l \end{matrix}\right\}\frac{\pi}{\alpha}q. \quad (7)$$

We may expect some difficulties in this connection.

In preparation for replacing the summation in Eq. (5) by integration, we rewrite:

$$\begin{aligned} a^l(q-Q_n)=(NL)^{-\frac{1}{2}}\{&\exp[\pi i(l-1)(q-Q_n)/\alpha] \\ &\times\sum_{m=0}^{N/2}\exp[2\pi im(q-Q_n)/\alpha N] \\ &+\exp[-\pi i(l-1)(q-Q_n)/\alpha] \\ &\times\sum_{m=0}^{N/2}\exp[-2\pi im(q-Q_n)/\alpha N]\}. \quad (8) \end{aligned}$$

We now replace summation over m by integration over dm, which is equivalent to going to infinite N and keeping the summation. The result is:

$$\begin{aligned} (NL)^{\frac{1}{2}}[2\pi i(q-Q_n)/N\alpha]a^l(q-Q_n) &=\{\exp[\pi i(l-1)(q-Q_n)/\alpha]\} \\ &\quad\times\{-1+\exp[\pi i(q-Q_n)/\alpha]\} \\ &\quad-\{\exp[-\pi i(l-1)(q-Q_n)/\alpha]\} \\ &\quad\times\{-1+\exp[-\pi i(q-Q_n)/\alpha]\}, \quad (9) \end{aligned}$$

$$\begin{aligned} a^l(q-Q_n)&=\alpha^{-\frac{1}{2}}[\alpha/\pi(q-Q_n)]\{\sin[l\pi(q-Q_n)/\alpha] \\ &\qquad-\sin[(l-1)\pi(q-Q_n)/\alpha]\} \quad (9\text{A}) \\ &=[2\alpha^{\frac{1}{2}}/\pi(q-Q_n)]\sin[\pi(q-Q_n)/2\alpha] \\ &\qquad\times\cos[\pi(l-\tfrac{1}{2})(q-Q_n)/\alpha]. \quad (9\text{B}) \end{aligned}$$

All this is a generalization of Wannier's original work[4] and agrees with it, of course, in the case of $l=1$ worked out by him. Wannier functions should have the property of orthonormality in the range $-\infty\leftrightarrow\infty$ for the indices l and n; this is shown to be the case in an appendix.

It is instructive to compare the Wannier functions for the lth band with the eigenfunctions of an electron in a box centered at Q_n with total length α. The lth such function is

$$\psi_l=\sqrt{2}\alpha^{-\frac{1}{2}}\cos[\pi l(q-Q_n)/\alpha]; \quad E_l=h^2l^2/8m\alpha^2. \quad (10)$$

Equation (9B) shows that the lth Wannier function is similar to Eq. (10); it has $(l-\frac{1}{2})$ in place of l and is modulated by $[(2\alpha)^{\frac{1}{2}}/\pi(q-Q_n)]\sin[\pi(q-Q_n/2\alpha]$. The energies of the lth band run from $h^2(l-1)^2/8m\alpha^2$ to $h^2l^2/8m\alpha^2$.

There is another choice of phases for the summation in Eq. (5) which leads to particularly simple results. In this choice, functions with $p_0>0$ are positive real at $q=0$; functions with $p_0<0$ are negative real at the origin. In this case Eq. (8) will have the plus sign connecting the summations in curly brackets replaced by minus sign, and Eqs. (9A) and (9B) become

$$\begin{aligned} a_-^l(q-Q_n)&=[\alpha^{\frac{1}{2}}/\pi i(q-Q_n)]\{\cos[\pi l(q-Q_n)/\alpha] \\ &\qquad-\cos[\pi(l-1)(q-Q_n)/\alpha]\}, \quad (9\text{A}') \end{aligned}$$

$$\begin{aligned} a_-^l(q-Q_n)&=[2i\alpha^{\frac{1}{2}}/\pi(q-Q_n)]\sin[\pi(q-Q_n)/\alpha] \\ &\qquad\times\sin[(l-\tfrac{1}{2})\pi(q-Q_n)/\alpha]. \quad (9\text{B}') \end{aligned}$$

We shall henceforth refer to the a's of Eqs. (9) as a_+ to distinguish them from a_- of Eqs. (9′). Since the sets $a_+(q-Q_n)$ and $a_-(q-Q_n)$ can be used to express the eigenfunctions of the same band, we expect to find a relation between them (probably correct up to terms of order $N^{-\frac{1}{2}}$). This relation, derived below, turns out to be valid in the general one-dimensional case and is not limited to the free-electron potential.

Let us try to express $a_-(q-Q_n)$ in terms of the set $a_+(q-Q_n)$. We see immediately that

$$a(q-Q_n)=N^{-\frac{1}{2}}\sum_{p_0}f(p_0)u_{p_0}(q)\exp(-ip_0\cdot Q_n/\hbar), \quad (11)$$

where $f(p_0)$ is plus one for $p_0>0$ and minus one for $p_0<0$, and the eigenfunctions u_{p_0} incorporate the phase choice of the original equations (9). In general,

$$u_{p_0}(q)=N^{-\frac{1}{2}}\sum_{Q_n}a_+(q-Q_n)\exp(ip_0\cdot Q_n/\hbar). \quad (12)$$

We substitute (12) into (11) to get

$$\begin{aligned} a_-(q-Q_n)=N^{-1}\sum_{Q_k}\sum_{p_0}&f(p_0)a_+(q-Q_k) \\ &\times\exp[ip_0\cdot(Q_k-Q_n)/\hbar]. \quad (13) \end{aligned}$$

Replacing the summation over p_0 by integration leads finally to

$$\begin{aligned} a_-(q-Q_n)=-i\sum_{Q_k}&a_+(q-Q_k) \\ &\times\{\cos[\pi(Q_k-Q_n)/\alpha]-1\}[\alpha/\pi(Q_k-Q_n)]. \quad (14) \end{aligned}$$

When we substitute our a_+ into Eq. (12), the result should be $u_{p_0}(q)$; if a_- is used, we should get $u_{p_0}(q)$ for $p_0>0$, $-u_{p_0}(q)$ for $p_0<0$, or $f(p_0)u_{p_0}(q)$. Before check-

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[4] G. H. Wannier, Phys. Rev. **52**, 191 (1937).

ing this, it is worth while to see what exceptions there might be. Suppose that our $a(q-Q_n)$ differs from the true Wannier function A by a term of order $N^{-\frac{1}{2}}$:

$$A^l(q-Q_n)=a^l(q-Q_n)+N^{-\frac{1}{2}}X. \tag{15}$$

X may be taken to be of the form

$$\sum_{d,p_0} c^d(p_0)u_{p_0}{}^d(q)\exp(-ip_0\cdot Q_n/\hbar). \tag{16}$$

In carrying out the operations of Eq. (12), we find that

$$u_{p_0}{}^l(q)=N^{-\frac{1}{2}}\sum_{Q_n} a^l(q-Q_m)\exp(ip_0\cdot Q_n/\hbar) +\sum_d c^d(p_0)u_{p_0}{}^d(q). \tag{17}$$

Hence, it may be that for certain p_0 (for which $c(p_0)\neq 0$),

$$N^{-\frac{1}{2}}\sum a^l(q-Q_n)\exp(ip_0\cdot Q_n/\hbar) =u_{p_0}{}^l(q)-\sum_d c^d(p_0)u_{p_0}{}^d(q). \tag{18}$$

In other words, the result of applying Eq. (12) to $a(q-Q_n)$ yields a result which is characterized by p_0, but it is not the normalized eigenfunction u_{p_0} unless all $c^d(p_0)=0$. This comes about because Eq. (12) picks up the term of order $N^{-\frac{1}{2}}$ in $a(q-Q_n)$; we have to be careful because we are in effect taking a sum of N terms of order $N^{-\frac{1}{2}}N^{-\frac{1}{2}}=N^{-1}$, and this sum need not vanish. It is plausible, however, to expect this sort of difficulty at only a finite number of points p_0 (a vanishingly small fraction of reciprocal space as $N\rightarrow\infty$), since our a's are actually orthonormal. If $c^d(p_0)$ were not a sum of δ functions around a limited number of p_0's, it would be hard to see how orthonormality could be preserved. Another way of putting this is that if $c^d(p_0)$ were different from zero over a finite range of p_0's, the term in X would no longer really be of order $N^{-\frac{1}{2}}$.

Keeping the discussion of the preceding paragraph in mind, we proceed to evaluate Eq. (12) for our a's at the points $p_0=0$, $h/2\alpha$, and $h/4\alpha$. Let $q/\alpha=x$, and $Q_n=n\alpha$. Then, for $p_0=0$,

$$N^{-\frac{1}{2}}\sum_n a_{\pm}{}^l(q-Q_n)=\frac{1}{(N\alpha)^{\frac{1}{2}}}\sum_n\frac{2}{\pi(x-n)} \times\sin[\tfrac{1}{2}\pi(x-n)]\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}[(l-\tfrac{1}{2})\pi(x-n)]. \tag{19}$$

Note that for even n

$$\sin[\tfrac{1}{2}\pi(x-n)]\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}[(l-\tfrac{1}{2})\pi(x-n)] =\sin(\tfrac{1}{2}\pi x)\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}[(l-\tfrac{1}{2})\pi x],$$

and for odd n it is given by

$$\cos(\tfrac{1}{2}\pi x)\left\{\begin{matrix}(-)^l\sin\\ (-)^{l-1}\cos\end{matrix}\right\}[(l-\tfrac{1}{2})\pi x].$$

It is therefore easy to break the summation of Eq. (19) into two parts to get

$$(N\alpha)^{-\frac{1}{2}}\tfrac{1}{2}\pi\left\{[\sum_{\text{even } n}(x-n)^{-1}]\sin(\tfrac{1}{2}\pi x)\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}[(l-\tfrac{1}{2})\pi x] +[\sum_{\text{odd } n}(x-n)^{-1}]\cos(\tfrac{1}{2}\pi x)\left\{\begin{matrix}(-)^l\sin\\ (-)^{l-1}\cos\end{matrix}\right\}[(l-\tfrac{1}{2})\pi x]\right\}.$$

We now make use of the relationships

$$\sum_r(x-2r)^{-1}=\tfrac{1}{2}\pi\cot(\tfrac{1}{2}\pi x),$$

$$\sum_r(x-1-2r)^{-1}=-\tfrac{1}{2}\pi\tan(\tfrac{1}{2}\pi x)$$

to evaluate the sums, and obtain[5]

$$\begin{aligned}(N\alpha)^{-\frac{1}{2}}&\left\{\cos(\tfrac{1}{2}\pi x)\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}[(l-\tfrac{1}{2})\pi x] -\sin\tfrac{1}{2}\pi x\left\{\begin{matrix}(-)^l\sin\\ (-)^{l-1}\cos\end{matrix}\right\}[(l-\tfrac{1}{2})\pi x]\right\}\\ &=(N\alpha)^{-\frac{1}{2}}\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}(l\pi x)\qquad\text{for } l \text{ even,}\\ &=(N\alpha)^{-\frac{1}{2}}\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}[(l-1)\pi x]\qquad\text{for } l \text{ odd.}\end{aligned}\tag{20}$$

The case of $h/2\alpha$ works out to

$$\begin{aligned}&(N\alpha)^{-\frac{1}{2}}\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}[(l-1)\pi x]\qquad\text{for } l \text{ even;}\\ &(N\alpha)^{-\frac{1}{2}}\left\{\begin{matrix}\cos\\ \sin\end{matrix}\right\}(l\pi x)\qquad\text{for } l \text{ odd.}\end{aligned}\tag{21}$$

For $p_0=h/4\alpha$, it turns out that the sums involved must be split up into four partial sums, and the final result is, for $l=1$, using either a_+ or a_-,

$$(N\alpha)^{-\frac{1}{2}}\exp(\tfrac{1}{2}\pi ix). \tag{22}$$

Equation (22) is the result we expect for almost all p_0's: it shows that Eq. (12) yields the true normalized eigenfunctions. The results summarized in Eqs. (21) and (22) are not normalized eigenfunctions; they lack a factor of $\sqrt{2}$. Moreover, it is clear that to get the result even proportional to the correct eigenfunction,

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[5] The author is indebted to Mr. T. O. Woodruff for pointing out this relationship.

a_+ must be used when the band-edge functions are cosines, and a_- when they are sines. At other p_0's it is immaterial whether a_+ or a_- is employed, but at $p_0=0$ and $h/2\alpha$, the terms in $N^{-\frac{1}{2}}$ make trouble.

In this connection it is of interest to see what happens when we use Eq. (14) to express a_- in terms of a_+ and then try to evaluate $u_{p0}(q)$ for $p_0=0$:

$$\begin{aligned} &N^{-\frac{1}{2}}\sum_n a_-(q-Q_n) \\ &=-iN^{-\frac{1}{2}}\sum_n\sum_k\frac{\{\cos[\pi(Q_k-Q_n)/\alpha]\}-1}{\pi(Q_k-Q_n)/\alpha}a_+(q-Q_n) \\ &=-iN^{-\frac{1}{2}}\sum_n\left\{\sum_k\frac{\cos[\pi(Q_k-Q_n)/\alpha]-1}{\pi(Q_k-Q_n)/\alpha}\right\}a_+(q-Q_n). \quad (23)\end{aligned}$$

This expression vanishes because the coefficient of $a_+(q-Q_n)$ is a sum over Q_k of terms which are odd in (Q_k-Q_n); thus each positive contribution is cancelled by an equal and opposite one. Under no circumstances can a_+ be made to express a sine function. When we try to force the issue, only zero emerges.

CHANGING THE LATTICE POINTS

One rather arbitrary feature of the definition of Wannier functions is the choice of the lattice points as the set $\{Q_k\}$. Let us see, in the general one-dimensional case, what the effect is of using the set $\{Q_k+\Delta\}$ instead. Begin by writing the one-electron eigenfunctions in terms of the Wannier functions defined using Q_k as the set of lattice points, as in Eq. (12). Let

$$\begin{aligned} a^\Delta(q-Q_n-\Delta)=N^{-\frac{1}{2}}\sum_{p_0} u_{p0}(q) \\ \times\exp[-ip_0\cdot(Q_n+\Delta)/\hbar]. \quad (24)\end{aligned}$$

Then

$$\begin{aligned} a^\Delta(q-Q_n-\Delta)=N^{-1}\sum_k\sum_{p_0} a(q-Q_k) \\ \times\exp[ip_0\cdot(Q_k-Q_n-\Delta)/\hbar]. \quad (25)\end{aligned}$$

Summation, or rather integration, over p_0 leads to:

$$a^\Delta(q-Q_n-\Delta)=\sum_k\frac{\sin[\pi(Q_k-Q_n-\Delta)/\alpha]}{\pi(Q_k-Q_n-\Delta)/\alpha}a(q-Q_k). \quad (26)$$

Extending Eq. (26) to three dimensions offers no difficulty.

The relation (26) illustrates the lack of uniqueness of the Wannier function definition. Another way to describe the situation is to regard Eq. (26) as the formula giving the new Wannier functions appropriate to a new choice of phases in which the phase of each u_{p0} is changed by $p_0\Delta/h$. The right-hand side of Eq. (26) appears highly delocalized, with contributions from Wannier functions centered at many points; but of course it is equal to the left-hand side, which contains just one Wannier function of the type a^Δ. A direct check of the last equation for our nearly-free-electron case is given in an appendix. Another possibility for the free-electron case is a phase change in each function given by $p\Delta/h$ rather than by $p_0\Delta/h$. The interesting relationships to which this choice leads are also dealt with in an appendix.

CHANGING UNIT CELL SIZE

Slater[6] has worked out the effect upon the Wannier functions of doubling the size of the unit length in a one-dimensional system. We shall cover approximately the same ground in this section; the freedom in manipulating Wannier functions given us by Eq. (26) makes it profitable to do so.

We have to begin with a system periodic with the period α. The Wannier function of the band which concerns us is $a(q-Q_n)$. The N different functions of q realizing by choosing $Q_n=n\alpha$ form a complete set for describing any function belonging to the band. If we now decide to double the unit cell, we will have two bands of functions spanning the same function space as our one original band. There will be $\frac{1}{2}N$ functions in each of these bands, so we see that what we are doing is just choosing another set of N linear combinations of the N original band functions. The Wannier functions for the new (half-) bands will be designated as $a^{\mathrm{I}}(q-Q_n)$ and $a^{\mathrm{II}}(q-Q_n)$, with only even values of n.

In the following equations, p_0 is a crystal momentum for the original description, and μ_0 is a crystal momentum in the double unit cell system:

$$a(q-Q_n)=N^{-\frac{1}{2}}\sum_{p_0=-h/2\alpha}^{h/2\alpha} u_{p0}(q)\exp(-ip_0\cdot Q_n/\hbar), \quad (27)$$

$$a^{\mathrm{I}}(q-Q_n)=(\tfrac{1}{2}N)^{-\frac{1}{2}}\sum_{\mu_0=-h/4\alpha}^{h/4\alpha} u_{\mu 0}'\exp(-i\mu_0\cdot Q_n/\hbar), \quad (28)$$

$$\begin{aligned} a^{\mathrm{II}}(q-Q_n)=(\tfrac{1}{2}N)^{-\frac{1}{2}}\sum_{\mu_0=-h/4\alpha}^{h/4\alpha} u_{\mu 0}''(q) \\ \times\exp(-i\mu_0\cdot Q_n/\hbar). \quad (29)\end{aligned}$$

Equation (27) is valid for all integral n; Eqs. (28) and (29) hold for even n only. We take $u_{\mu 0}'=u_{p0=\mu 0}$ and $u_{\mu 0}''=u_{p0=\mu 0\pm h/2\alpha}$ using the plus sign for $\mu_0>0$ and the minus sign for $\mu_0<0$. We note that the periodic boundary condition (P.B.C.) gives $[m/(N/2)]/(h/2\alpha)=mh/N\alpha$ as the allowed values of μ_0; hence, μ_0 assumes the same values as p_0 below $|\mu_0|=h/4\alpha$. Consideration of the foregoing relations shows fairly directly that

$$a(q-Q_n)=2^{-\frac{1}{2}}[a^{\mathrm{I}}(q-Q_n)+a^{\mathrm{II}}(q-Q_n)], \quad n \text{ even}; \quad (30)$$

$$a(q-Q_n-\alpha)=2^{-\frac{1}{2}}[a^{\mathrm{I}}(q-Q_n-\alpha)-a^{\mathrm{II}}(q-Q_n-\alpha)], \quad n \text{ even}. \quad (31)$$

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[6] J. C. Slater, Phys. Rev. **87**, 807 (1952).

Note especially the sign of a^{II} in Eq. (31), which is what takes account of the difference between p_0 and μ_0. The expression $a^{\mathrm{I}}(q-Q_n-\alpha)$ is to be interpreted as the function obtained from Eq. (28) by replacing Q_n with $Q_n+\alpha$. Obviously, $a(q-Q_n-\alpha)$ is equal to $a(q-Q_{n+1})$, which could be shown formally from Eq. (26). We can also use Eq. (26), modified for the double periodicity, to express the right-hand side of Eq. (31) in terms of the set with even n:

$$a(q-Q_{n+1})=2^{-\frac{1}{2}}\sum_{\text{even }k}\left[a^{\mathrm{I}}(q-Q_k)-a^{\mathrm{II}}(q-Q_k)\right]\times\{\exp[\tfrac{1}{2}\pi i(k-n)]\}[2/\pi(k-n-1)]. \quad (32)$$

Equations (30) and (32) show us how to express the N Wannier function of the full band in terms of the 2 times $\frac{1}{2}N$ Wannier functions for the two half-bands, defined for even n only.

The converse problem, that of expressing a^{I} and a^{II} in terms of a, can be handled by expanding the former in series of the latter, using Eqs. (30) and (32) to evaluate the coefficients:

$$a^{\mathrm{I},\mathrm{II}}(q-Q_n)=2^{-\frac{1}{2}}\sum_{\text{even }r}\left[\delta_{rn}a(q-Q_r)\pm a(q-Q_{r+1})\frac{\exp[\frac{1}{2}\pi i(n-r)]}{\frac{1}{2}\pi(n-r-1)}\right]. \quad (33)$$

We use the plus sign in expanding a^{I} and the minus sign for a^{II}. We see very clearly that the reason for the appearance of Wannier functions from many sites in the expansion is our exclusion of half-band functions at other than even lattice points and our subsequent use of Eq. (26) to transform these away.

SYMMETRY PROPERTIES OF WANNIER FUNCTIONS

Our aim in this section is to see what can be said about Wannier functions on the basis of crystal symmetry. Previous work in this direction has been done by Slater,[6] Koster,[7] and Feuer.[8]

The definition of Wannier functions shows that they are linear combinations of eigenfunctions. Since the eigenfunctions belong to irreducible representations of the space group of the crystal, it appears that Wannier functions could be classified symmetry-wise by specifying just which irreducible representations (I.R.) of the space group characterize the eigenfunctions of the band. Another kind of symmetry characterization which might be desirable is a specification of the behavior of a Wannier function under the symmetry operations which leave invariant the point about which it is localized.

It is convenient to begin with a one-dimensional example which exhibits some of the results without complicated geometry. A case at hand is our nearly-free-electron one, which will have a space group involving translations by multiples of α along the line, and reflections in lines perpendicular to the line of the crystal at points $\frac{1}{2}n\alpha$, with n any integer. Consider the case in which the (P.B.C.) is applied to a region of the line N unit cells long. No real loss in generality is involved in assuming that N is even. Any operation of the group may be expressed in the form $\{R|\mathbf{t}\}$, where R is either the identity or a reflection in the origin, and $\mathbf{t}$ is a translation $n\alpha$. On account of the P.B.C., operations which leave the line translated by $N\alpha$ from its position at the end of a given operation are considered to be the same as the given operation. All pure translations are of the form $\{E|n\alpha\}$, and $\{E|(n+N)\alpha\}$ is the same as $\{E|n\alpha\}$. Reflections are of two types; those which leave invariant a point translationally equivalent to the origin, of the form $\{\sigma|n\alpha\}$ with n even; and those which leave invariant the points translationally equivalent to $\frac{1}{2}\alpha$, of the form $\{\sigma|n\alpha\}$ with n odd. It is to be noted that $\{\sigma|n\alpha\}$ and $\{\sigma|(n+N)\alpha\}$ are to be regarded as the same operation, since they differ only in that the line is translated by $N\alpha$ after one of these operations with respect to its position after the other. This (or these) operation(s) leaves invariant two points, at $\frac{1}{2}n\alpha$ and at $\frac{1}{2}(n+N)\alpha$.

We can get at the symmetry properties of a band by considering the character system of the reducible representation for which its functions provide a basis. These character systems are represented in Table I for some interesting cases. The four rows of entries are for, respectively, the set of even Wannier functions for a band, the set of odd Wannier functions, the set of eigenfunctions of a band for which the band-edge functions are cosines, and the set of eigenfunctions with sine-type band-edge functions. The character entries are obtained simply, as follows: $\chi(E)$ is N for all four sets since they all contain N functions. The functions a_+ and a_- are translated into others of the set by any translation, and hence have zero character for translation. Two of them are left invariant (for a_+) or have their sign changed (a_-). The other kind of reflection interchanges members of the set. The effect of a translation on any u_{p0} is to multiply it by $\exp(ip_0\cdot t/\hbar)$. This number becomes a diagonal element of the matrix representing the translation; the sum of these diagonal elements is the character, and this sum vanishes. Any reflection in points equivalent to the origin interchanges functions of the sets u_{p0} contributing nothing to the character, except for the two band-edge functions. These are left invariant [for u_{p0}(cos)], contributing two, or change sign [for u_{p0}(sin)], contributing minus two to the character. A similar argument shows that the contribution to the character for the other type of reflection and for the sets u_{p0} vanishes for all but the band-edge functions, and the upper and lower band-edge functions give equal and opposite diagonal elements, so that the total is zero.

One kind of set of u_{p0} which has apparently been neglected is that with one cosine-like and one sine-like

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[7] G. F. Koster, Phys. Rev. 89, 67 (1952).

[8] P. Feuer, Phys. Rev. 88, 92 (1952).

TABLE I. Some characters for reducible representations of the linear translation group with reflection.

Basis function	$\{E\|0\}$	$\{E\|n\alpha\}$	even n $\{\sigma\|n\alpha\}$	odd n $\{\sigma\|n\alpha\}$
a_+	N	0	2	0
a_-	N	0	-2	0
u_{p_0}(cos-like)	N	0	2	0
u_{p_0}(sin-like)	N	0	-2	0

band-edge function. Actually, this kind of set is included already if we reverse the roles of the two types of reflection, which corresponds to moving the origin from the initial position to the mid-point of the first unit cell. This kind of set could have a sine-like upper-edge function and cosine-like lower one, or *vice versa*. The four possibilities correspond to the four possibilities for band-edge functions discussed originally by Shockley[9] (see Feuer[8]).

The appropriate kind of Wannier functions to go with each of these kinds of bands is easily determined by comparing characters. We note the fact which we have already used, that a_+ is even with respect to reflection at its center, and a_- is odd. Then the set a_+ goes with u_{p0}(cos) and a_- with u_{p0}(sin), as these sets have the same characters. Similarly, if we have cos-sin or sin-cos bands, the appropriate Wannier functions would be a_+-like or a_--like, centered at points translationally equivalent to $\frac{1}{2}\alpha$.

If we are willing to give up the ability of the Wannier functions to produce the band-edge eigenfunctions when substituted into Eq. (12) requiring only that u_{p0} with p_0 different from zero or $h/2\alpha$ be properly rendered, then we have no symmetry requirement at all on the Wannier function. They can be either odd or even, or a linear combination of odd and even functions about the center of localization. An example of this sort of thing occurred when we were able to express a_- in terms of a_+ —only the band-edge function gave difficulty in that case. The result is trivial when we recognize that the functions of a band have no symmetry properties which distinguish them from other bands except for the symmetry properties of the band-edge functions. However, it points the way to an understanding of similar but more complicated situations which arise in two- and three-dimensional cases.

In two and three dimensions, situations occur which make it difficult to assign energies to bands—there is a sticking together of bands so that, in effect, one energy may belong to several bands. We wish to settle what restrictions, if any, there may be on the symmetry behavior of a Wannier function of a band of energy levels in a multidimensional crystal. The general case would be rather complicated to carry through, but the kind of result to be expected will be clear from the discussion of a special case, already treated from a somewhat different point of view by Slater[6] and Koster.[7] This special case is a square lattice with a potential given by the sum of Mathieu potentials in x and y, plus a small perturbation. The $0-1$ and $1-0$ bands are degenerate, and mix under the perturbation to give us a situation like that mentioned in the last paragraph, in which the bands stick together at the center and corners of the Brillouin zone.

It is easy to see that in this case one may choose to represent this pair of bands a pair of Wannier functions which belong to a degenerate representation of the group C_{iv} of the "atomic" sites, since these are in fact the functions with which the analysis of Slater and Koster began. These degenerate functions are not correlated with the individual bands; it takes both Wannier functions to express an eigenfunction of either band. Slater and Koster go on to show how nondegenerate Wannier functions can be formed, each of which will yield by itself, under proper operations, the functions of one band. The point which is not clear so far is how on the one hand a pair of degenerate functions, and on the other a nondegenerate pair, can give the same bands of eigenfunctions. The resolution of the difficulty lies in perceiving that they really do not. Consideration of Slater's[6] Eq. (51) and Table VI indicates that just at the corners and center of the Brillouin zone the nondegenerate Wannier functions produce not the appropriate eigenfunction, but zero. We have a situation like that which we have seen already in the one-dimensional case, when the result of using a Wannier function of the "wrong" symmetry is to have the expression for an eigenfunction at some special $\mathbf{p}_0$ yield zero. This circumstance is also reminiscent of the redundant coordinates which appear in the theory of molecular vibrations. Our conclusion is that we can indeed have nondegenerate Wannier functions if we are willing to give up their ability to reproduce the sticking-point eigenfunctions. This is very much in accord with the considerations of Bouckaert, Smoluchowski, and Wigner,[10] who feel that the definition of a band of energy levels should exclude the sticking-point levels.

Slater's and Koster's nondegenerate Wannier functions do, however, retain the ability to yield the eigenfunction (at least to within a nonzero factor) at points reciprocal space lying on symmetry planes or axes. If this property is given up, then there would be no symmetry restriction at all on the Wannier functions.

RELATION BETWEEN SITE SYMMETRY AND SPACE GROUP SYMMETRY

We intend to show some of the relations between crystal orbital theory and site orbital theory which arise from symmetry and which are of great value in transferring ideas from one theory to the other. The argument can be put in a form applicable to either molecules or crystals; it represents an improvement of

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[9] W. Shockley, Phys. Rev. **56**, 317 (1939).

[10] Bouckaert, Smoluchowski, and Wigner, Phys. Rev. **50**, 58 (1936).

a method due to Hall[11] in that here account is taken on the representation of the site group to which the SO belongs. We consider a set of SO, each belonging to the representation γ_j of its site group. If the representation is degenerate we include all the partners. We seek to find which irreducible representations Γ_i of the molecular or crystal (space) group span the reducible representation for which our SO form a basis. We proceed by finding the character $\Xi(R)$ of this reducible representation for each operation of the molecular or crystal group. For a given operation there is a contribution of $\chi_j^{\text{s.g.}}(R)$ for each site left invariant by the operation, where $\chi_j^{\text{s.g.}}(R)$ is the character for R in the jth site group representation; otherwise the contribution is zero.

$$\Xi(R)=\sum_\alpha \delta_\alpha(R)\chi_j^{\text{s.g.}}(R). \quad \delta_\alpha=1 \text{ if } R \text{ is in site group of the } \alpha\text{th site; } \delta_\alpha=0 \text{ otherwise.} \tag{34}$$

We then reduce this representation to find which irreducible representations contribute to it. If $\Xi_i(R)$ is the character of R in Γ_i, we have for the number of times Γ_i appears in the reducible representation

$$^in_i=(1/H)\sum_R \Xi_i^*(R)\Xi(R), \tag{35}$$

where H is the order of the molecular or space group. We substitute for $\Xi(R)$ from Eq. (34) and use the relationship (36), based on the site group's being a subgroup of the molecular or crystal group, to obtain Eq. (37). As Eq. (36b) shows, the a_{ik} are easy to determine once the character tables of the two groups are known:

$$\left.\begin{aligned}\Xi_i(R)&=\sum_k a_{ik}\chi_j^{\text{s.g.}}(R), && \text{(36a)}\\ a_{ik}&=h^{-1}\sum_R \chi_k^{*\text{s.g.}}(R)\Xi_i(R), && \text{(36b)}\end{aligned}\right\} R \text{ in site group.}$$

$$^in_i=H^{-1}\sum_\alpha\sum_R\sum_k a_{ik}\chi_k^{*\text{s.g.}}(R)\chi_j^{\text{s.g.}}(R)\delta_\alpha(R), \tag{37}$$

$$^in_i=a_{ij}. \tag{38}$$

Equation (38) arises from application of the orthogonality relations for group characters and the definition of $\delta_\alpha(R)$ to get for the summation over R and k the value of $a_{ij}h$, where h is the order of the site group and equal to H divided by the number of equivalent sites in the set. Summing over α leaves Eq. (38). This group theoretical argument has been used earlier by the author[12] for similar purposes. Equation (38) tells us which irreducible representations of the crystal or molecular group are included in the representations induced by SO belonging to the jth site group representations located on the sites α, and hence provides a way to translate the symmetry properties of a site treatment into those of a molecular or crystal orbital treatment. As an example of the application of (38) we may determine the number of times any F-dimensional representation of the space group (F is the order of its factor group) appears in the space group representation induced by a set of SO centered on sites of symmetry C_1. From Eq. (36b) a_{ij}, and hence ^in_i, is obviously $(1/1)\chi_1^{C_1}(E)\Xi_i(E)$, or just F.

A converse problem is the determination of the kind of SO which may be constructed if we know that we have molecular or crystal orbitals belonging to Γ_i. In crystals the problem will be nontrivial only when Γ_i is a representation for some special value of $\mathbf{p}_0$ at which the star is degenerate. Possible candidates for SO must be those belonging to such representations γ_j that a_{ij} does not vanish; we can easily determine these by running through all representations of all kinds of sites. Whether the SO going with such j can actually be constructed is further determined by whether we have molecular or crystal orbitals belonging not only to Γ_i but also to Γ_k for all nonzero a_{kj}. Functions of Γ_i need the cooperation of functions in the other representations Γ_k in order that linear combinations of them belonging to γ_j may be set up.

A point worth mentioning is that sites are not necessarily only the loci of atoms in a molecule or crystal. Any point in space is a site with a site group of at least C_1 symmetry. Of course, the more symmetry there is around a site, the finer is the symmetry classification of functions centered at it.

The kind of symmetry information which is given us by the knowledge that we have a set of SO of a certain site symmetry on a set of sites is quite similar, we see from Eq. (38), to information about the symmetry of molecular orbitals or, in crystals, to information about the representations of band functions at special points in crystal momentum space. Further, the SO information is so much more closely related to chemical notions that it may be much more valuable to have the symmetry information in the SO form. In the diamond lattice, for instance, it is much more revealing to know that the valence band functions can be represented by SO (here they are also EO) which are symmetric with respect to inversion at the inversion centers midway between atoms and, hence, are of a binding character than it is to know the complete reduction of the space group representation of these orbitals. Likewise, valuable insight into the conduction band orbitals can be obtained from the "chemical" kind of information that the corresponding SO are antibonding, having a node between atoms required by their antisymmetry under inversion.

EQUIVALENT ORBITALS IN METALS

It seems worth while to see what can be said about metals. The distinguishing characteristic of metals in the band theory is that they do not have filled bands and, hence, it is difficult to define EO for them. However, the artifice of introducing a superlattice, which in turn divides up the Brillouin zones for the original

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[11] G. G. Hall, Proc. Roy. Soc. (London) **A202**, 323 (1950).

[12] H. Winston, J. Chem. Phys. **19**, 156 (1951).

lattice, always makes it possible just to include all the occupied crystal orbitals in filled zones of the superlattice. The idea is applicable to ferromagnetic as well as to ordinary metals to the extent that the ground states can be represented by single antisymmetrized determinants. Whether the artifice has any value for quantitative investigations depends on how big the superlattice has to be made; evidently a superlattice so large that one cell of it encompassed the whole crystal would have its zones filled, but it would not simplify things at all. A point of qualitative interest is that the superlattice can be superimposed upon the original lattice in a number of ways equal to the number of original unit cells in one supercell. Going with each of these ways are sets of sets of EO. As Lennard-Jones[2] has shown, the possibility of defining sets of EO in more than one way (as for the π orbitals of benzene) arises in situations where other valence theories would invoke the concept of resonance. Since each of the EO so defined will be spread over many atoms (at least the whole super-cell), we seem to have a parallel to Pauling's ideas[13] on the electronic structure of metals, which are based on an entirely different staring point.

SITE ORBITALS AND PERTURBED LATTICES

SO have a special value in the theory of perturbed lattices. The methods of Peckar[14] and Slater,[1] which use the crystal eigenfunctions or the Wannier functions of one band of the unperturbed lattice as basis functions for a perturbation calculation, are legitimate as long as the perturbation is small compared to the energy separation between bands. This restriction is not satisfied in many practical cases in which degenerate bands occur or where the perturbation is comparable to the separation between nondegenerate bands. Adams[15] has provided a formalism for taking into account as many bands of the unperturbed lattice as may be necessary to expand the perturbed eigenfunctions. We propose a restatement of his method in terms of SO, which has the advantage that SO are generally much easier to visualize than Wannier functions in three dimensions. As in general the SO are linear combinations of Wannier functions, no more than a linear transformation of Adams' equation is necessary to put it in the SO form.

We can discuss qualitatively the perturbation caused by the removal of an atom from a diamond lattice, leaving a vacancy or Schottky defect. The perturbation is very large, compared even to the valence-conduction edge separation. A first approximation would consist of the use of the valence band SO's, localized functions which are even with respect to inversion at the inversion centers of the crystal and which correspond to the chemical idea of bonds. We see immediately, though, that limiting ourselves to expansions in these SO is found to be unsatisfactory, because the complete wave function will be unable to take full account of changes within an atomic distance of the vacancy, limited as it is by the form of the SO. In this case it seems profitable to supplement our basis functions by the SO for the conduction bands, which are odd under inversion. Now the exigencies of the perturbation can cause variations in the relative amounts of odd and even orbital on the sites surrounding the vacancy, and the result is likely to be much more realistic. If convenient, the odd and even SO could be combined to form one set of new SO, placed at points along the interatomic axes not on the inversion center but symmetrically located with respect to it. There will be four such SO nearer each atom than any other. They will be rather like the directed orbitals of a hypothetical carbon atom in space and will be well suited to describing the situation at vacancy, where we may well expect the electronic structure at the neighboring atoms to revert to something like a free-space arrangement.

SPECULATION ON STRUCTURE OF CdSb

Semiconductors are characterized by possessing filled bands, with not too large an energy gap before the next empty band. It is not always easy to see why the energy gaps should come as they do. However, to the extent that we can characterize bonds by the corresponding EO, we can make sense of a filled band structure if it corresponds to a set of filled bonding EO, and if the next SO to be filled are obviously of higher energy. This notion is implicit in the work of Hall on the diamond structure.

The crystal structure of CdSb and ZnSb has been determined by Almin.[16] These semiconducting compounds contain sixteen atoms per unit cell, arranged so that there are twenty-eight interatomic distances corresponding to Sb—Sb bonds and Cd—Sb (or Zn—Sb) bonds. There are also four interatomic distances corresponding to Cd—Cd (or Zn—Zn) bonds. The Cd—Cd, but not the Zn—Zn, distance is significantly larger than can be accounted for by Pauling's atomic radii, according to Almin. We thus expect that the Cd—Cd bonds would have higher energies than the other twenty-eight bonds, and we observe that these other twenty-eight bonds are just filled by the fifty-six valence electrons of the sixteen atoms in the unit cell. The Zn—Zn distance is not indicative of a higher than usual Zn—Zn bond energy, but we can still argue that the Zn—Zn bond is different from the other twenty-eight bonds and very likely has a higher energy even at its normal distance. In each case, then, we can qualitatively assign all the electrons to a set of low-lying bonds, leaving the next higher ones empty. This illustrates the maxim that filled bands imply filled bonds, and vice versa.

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[13] L. Pauling, Nature **161**, 1019 (1948); Physica **15**, 23 (1949).

[14] S. Peckar, J. Phys. (U.S.S.R.) **10**, 431 (1946).

[15] E. N. Adams II, Phys. Rev. **85**, 41 (1952).

[16] K. E. Almin, Acta Chem. Scand. **2**, 400 (1948).

APPENDIX

We find directly the relation between $a_{\pm}^{l\Delta}(q-Q_n-\Delta)$ and $a_{\pm}^{l}(q-Q_k)$ for the nearly-free electron case by writing an expression for the former and expanding it in a series of the latter. For simplicity we will write the a's as $a^{\Delta}(q-Q_n-\Delta)$ and $a(q-Q_k)$, letting the l and $\pm$ be understood. Equation (A1) is derived in the same way as Eq. (9).

$$a^{\Delta}(q-Q_n-\Delta)=(-)^{l-1}\alpha^{-\frac{1}{2}}\frac{\sin\{\pi[l(q-Q_n)-\Delta]/\alpha\}-\sin[\pi(l-1)(q-Q_n)/\alpha]}{\pi(q-Q_n-\Delta)/\alpha}. \tag{A1}$$

Now, $a^{\Delta}(q-Q_n-\Delta)$ can be expanded in series of the orthonormal set $a(q-Q_k)$ for the same band. Determination of the expansion coefficients involves evaluation of the integrals

$$\int dq a^{\Delta}(q-Q_n-\Delta)a(q-Q_k),$$

a long-winded but straightforward process. The result for this coefficient is

$$(-)^{l-1}\frac{\sin\{\pi[l(Q_k-Q_n)-\Delta]/\alpha\}-\sin[\pi(l-1)(Q_k-Q_n)/\alpha]}{\pi(Q_k-Q_n-\Delta)/\alpha}. \tag{A2}$$

A little trigonometric manipulation shows that Eq. (A2) is in agreement with Eq. (26). Writing it in this form, however, brings out the fact that the coefficient is, to within a factor of $\alpha^{-\frac{1}{2}}$, the same function of (Q_k-Q_n) that a^{Δ} is of $(q-Q_n)$ in Eq. (A1).

If we define $a^{\Delta\prime}(q-Q_n-\Delta)$ as the free electron Wannier function with the phases so chosen that all eigenfunctions are positive real at the point Δ, then obviously $a^{\Delta\prime}(q-Q_n-\Delta)$ is the same function of $(q-Q_n-\Delta)$ that a $(q-Q_n)$ is of $(q-Q_n)$.

$$a^{\Delta\prime}(q-Q_n-\Delta)=\alpha^{-\frac{1}{2}}\frac{\sin[l\pi(q-Q_n-\Delta)/\alpha]-\sin[(l-1)\pi(q-Q_n-\Delta)/\alpha]}{\pi(q-Q_n-\Delta)/\alpha}. \tag{A3}$$

As before, the coefficients in the expansion of $a^{\Delta\prime}$ in terms of the a's can be readily evaluated. The coefficient of $a(q-Q_k)$ in the expansion of $a^{\Delta\prime}(q-Q_n-\Delta)$ is

$$\frac{\sin[l\pi(Q_k-Q_n-\Delta)/\alpha]-\sin[(l-1)\pi(Q_k-Q_n-\Delta)/\alpha]}{\pi(Q_k-Q_n-\Delta)/\alpha}. \tag{A4}$$

Again, (A4) is of the same form, except for the factor $\alpha^{-\frac{1}{2}}$, as $a^{\Delta\prime}$ itself in (A3).

The orthogonality properties of the nearly-free-electron Wannier functions can be worked out in terms of the integral

$$\mathcal{I}(l,s;m,n)\equiv\int a_+^{l}(q-Q_m)a_+^{s}(q-Q_n)dq. \tag{A5}$$

Upon letting $q-Q_m=x$, and $q-Q_n=q-Q_m+(Q_m-Q_n)=x+(m-n)\alpha$, and defining $F(l,s;m-n)$ as

$$\frac{1}{\alpha}\int_{-\infty}^{\infty}dx\frac{[\sin(\pi lx/\alpha)]\sin\{\pi s[x+(m-n)\alpha]/\alpha\}}{\pi^2x[x+(m-n)\alpha]/\alpha^2},$$

we have

$$\begin{aligned}\mathcal{I}(l,s;m,n)=&F(l,s;m-n)+F(l-1,s-1;m-n)\\&-F(l,s-1;m-n)-F(l-1,s;m-n).\end{aligned} \tag{A6}$$

We can evaluate the F function as follows:

$$F(l,s;r)=[\sin(\langle l,s\rangle r\pi]/r\pi, \tag{A7}$$

where $\langle l,s\rangle$ denotes the smaller of l and s; we get, for $l\leqslant s-1$,

$$\mathcal{I}(l,s;m,n)=0,\quad\text{independent of } m \text{ and } n. \tag{A8}$$

For $l=s$ we have

$$\mathcal{I}(l,l;m-n)=\delta_{m,n}. \tag{A9}$$

The preceding equations imply $\mathcal{I}(l,s;m,n)=\delta_{l,s}\delta_{m,n}$, as required for orthonormality.