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Comparison of Standard and Modified Orthogonalized Plane-Wave Methods

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We compute electron energy levels for some selected irreducible representations of two crystals, Cu and $LaSn_3$, using both the standard orthogonalized plane-wave method (OPW) and a modified form of this method (MOPW). It is shown that (for a nonrelativistic non-self-consistent treatment, at least) the convergence, in the sense of the number of symmetrized plane waves required, is both more rapid and more reliable for MOPW than for OPW. For the two crystals chosen, standard OPW was found to be reasonably good for $LaSn_3$ but inadequate for Cu, whereas MOPW was quite adequate for both.

I. INTRODUCTION

The standard orthogonalized plane-wave (OPW) method developed by Herring[1] has enjoyed a large measure of success in electronic band-structure calculations. It is fairly well known, however, that in standard form OPW does not work well for certain crystals,[2] particularly the transition elements where the *3d* shell is being filled or Cu with a just-filled *3d* shell. In such elements the *3d* atomic function is generally not a reasonably accurate eigenfunction for the crystal. Thus, orthogonalizing to this function or to an atomic-like function constructed from it generally leads to poor results. If, on the other hand, the *3d* atomic function is ignored completely, a large number of symmetrized plane waves will be required for convergence.

Brown and Krumhansl[3] developed a method which avoids such difficulties by treating all the atomic-like functions as expansion functions on the same footing as the plane waves. In this modified plane-wave (MPW) method, the plane waves are not orthogonalized to any of the atomiclike functions. The MPW method has been used by Brown and Krumhansl[3] for Li and by Butler *et al.*[4] for Cu to give a few examples. The last-named paper is of particular importance in establishing the MPW method as the results are in extremely good agreement with the calculations on Cu by Burdick,[5] who used the augmented plane-wave (APW) method. Both Burdick and Butler *et al.* used the Chodorow[6] potential.

II. MOPW METHOD

We now describe a method which combines features of the MPW and OPW methods. We refer to this as a modified orthogonalized plane-wave (MOPW) method. In this method, the symmetrized plane waves are orthogonalized only to those lower-lying atomic functions (in the form of symmetrized Bloch sums) which one "trusts" as being quite good crystal eigenfunctions as well. The plane waves are not orthogonalized to the higher atomiclike functions. These higher atomiclike functions are kept in the expansion explicitly as symmetrized Bloch sums on the same footing as the (symmetrized) orthogonalized plane waves. Our procedure is essentially the same as that of Deegan and Twose,[7] differing mainly in the manner of obtaining the atomiclike functions. A somewhat similar approach was used by Callaway[8] in a calculation for iron. This idea of supplementing the orthogonalized plane waves with functions picked to represent the appropriate atomic function symmetries is not a new one, having already been suggested by Herring[1] in his original OPW paper. Brown[9] has shown that MOPW is mathematically identical to MPW if the atomic functions to which one orthogonalizes are exact eigenfunctions for the crystal. An outline of our version of MOPW is given in the Appendix.

III. COMPARISON OF MOPW AND OPW

We felt it would be appropriate to compare MOPW and standard OPW for an actual case. We confine ourselves here to three irreducible representations of Cu and two of $LaSn_3$.[10] For this comparison we take the MPW results as being "correct," since, of the three methods (MPW, MOPW, and OPW), MPW has the highest degree of variational flexibility.

For both Cu and $LaSn_3$ a muffin-tin model was used. The same Chodorow[6] potential used by Burdick[5] and by Butler *et al.*[4] was used for Cu while the $LaSn_3$ crystal potential was constructed from the atomic potentials for La and Sn of Herman and Skillman.[11] These La and Sn potentials were modified slightly near the muffin-tin radii so as to join smoothly along a line connecting the La and Sn nuclei. The atomiclike functions were determined by solving the Schrödinger equation for the appropriate atoms using the above potentials. These solutions contain the added restriction that the functions go to zero with zero slope by the radius of the appropriate muffin-tin sphere. For the higher-lying atomic levels, these truncated functions have somewhat higher energies than the corresponding free-atom functions.

A. Selected Irreducible Representations for Cu

X_4': $\vec{k} = (100)$.[12,13] This representation allows p symmetry only. The Cu atomiclike $2p$ and $3p$ levels are at approximately − 65.9 and − 5.4 Ry, respectively. The Cu Fermi level is at − 0.38 Ry.[5]

Table I lists electron energy levels for four choices of calculation. In Tables I–V, column 1 gives the number of symmetrized plane waves used in a particular truncation, column 2 lists the square of the magnitude[13] of the largest plane wave in that particular truncation of the matrix equation, and column 3 gives the MPW energy level. All energies are in Ry. Retention of the fourth decimal place in the energies listed is merely to show comparison. In Tables I–V, only the energy levels of interest are shown. In Table I, MOPW orthogonalizes to $2p$ and "keeps" $3p$ as an explicit expansion function; i.e., we do not orthogonalize to the $3p$ atomiclike function. OPW1 orthogonalizes to $2p$ and $3p$. OPW2 orthogonalizes to $2p$ and ignores $3p$.

As expected, MOPW is virtually identical to MPW. This, plus the fact that the orthogonalized plane waves do contribute importantly to this level, indicates merely that the Cu $2p$ atomic function is an accurate eigenfunction for the crystal. Orthogonalizing to $3p$ (OPW1) produces a level which is consistently low by about 0.01 Ry. At −5.4 Ry, the atomiclike $3p$ function is probably a quite good eigenfunction for the crystal. Ignoring the $3p$ function (OPW2) produces levels which converge quite slowly.

TABLE I. $X_{4'}$ energy levels for Cu. See text for a description of the various methods of calculation. All energies are in Ry. For reference, Burdick's APW level is at −0.235 Ry (Ref. 5).

Symmetrized plane waves	Magnitude squared	MPW[a]	MOPW	OPW1	OPW2
1	1	−0.2151	−0.2151	−0.2250	
6	13	−0.2335	−0.2336	−0.2428	
12	22	−0.2345	−0.2346	−0.2436	0.2053
18	30	−0.2346	−0.2346		
24	38	−0.2347	−0.2346	−0.2435	−0.0752
38	54			−0.2439	−0.1702

[a] The MPW level at 24 plane waves is from Butler *et al.* (Ref. 4). The other MPW levels (and the fourth significant figure of the 24 plane-wave level) are from Butler (private communication). We recalculated the 1 and 12 plane-wave levels as a check: They agree to four significant figures with those of Butler.

Table II. $\Gamma_{25'}$ energy levels for Cu. All energies are in Ry. For reference, Burdick's APW level is at −0.640 Ry (Ref. 5).

Symmetrized plane waves	Magnitude squared	MPW[a] and MOPW	OPW1	OPW2
1	3	−0.6220		
6	19	−0.6339		
12	27	−0.6411	1.575	0.644
24	44	−0.6453	1.574	0.493
38	59	−0.6465	1.572	0.370

[a]The MPW level at 24 plane waves is from Butler *et al.* (Ref. 4). The other MPW levels (and the fourth significant figure of the 24 plane-wave level) are from Butler (private communication).

$\Gamma_{25'}$: $\vec{k} = (000)$. This representation allows d symmetry only. The Cu atomiclike $3d$ level is at about − 0.5 Ry. Here MOPW and MPW are identical procedures since the only atomic function involved is the $3d$, and MOPW would keep this as an expansion function.

Table II lists energy levels for three choices of calculation. OPW1 orthogonalizes to $3d$. OPW2 ignores $3d$. In Tables II–V, the column labeled OPW1 is included mainly for completeness. Since one of the atomiclike functions to which we orthogonalize in OPW1 in Tables II–V is a major contributor to the desired level, one would not expect good results with this choice of computation.

From Table II it is clear that standard OPW (either orthogonalizing to $3d$ or ignoring $3d$) does not give good results for $\Gamma_{25'}$. Similar results (not shown) were obtained for X_5 which also allows only d symmetry.

Σ_4: $\vec{k} = (\frac{1}{4}, \frac{1}{4}, 0)$. This representation allows p and d symmetry. Table III lists energy levels for five choices of calculation. MOPW orthogonalizes to $2p$ and keeps $3p$ and $3d$. OPW1 orthogonalizes to $2p$, $3p$, and $3d$. OPW2 orthogonalizes to $2p$ and $3p$ and ignores $3d$. OPW3 orthogonalizes to $2p$ and ignores $3p$ and $3d$.

From Table III we see that orthogonalizing to the $3d$ function is unsuitable (OPW1) and that ignoring the $3d$ (OPW2 or OPW3) produces extremely slow convergence. The $3d$ function contributes very strongly to the level of interest in Σ_4, so that OPW does not give good results here as it did for $X_{4'}$ where only p symmetry was involved. MOPW gives results which are identical (to four figures) to MPW.

TABLE III. Σ_4 $(\frac{1}{4}, \frac{1}{4}, 0)$ energy levels for Cu. All energies are in Ry. For reference, Burdick's APW level is at −0.600 Ry (Ref. 5).

Symmetrized plane waves	Magnitude squared	MPW	MOPW	OPW1	OPW2	OPW3
1	3.125	−0.4936[a]	−0.4936			
6	9.125	−0.5769	−0.5769		1.188	
12	13.125	−0.5863	−0.5863	1.599	1.029	1.030
18	18.125	−0.5879	−0.5879			
26	21.125	−0.5888		1.592	0.921	0.924
36	27.125			1.591	0.848	0.850

[a] This level is from Butler (private communication).

B. Selected Irreducible Representations of $LaSn_3$

$LaSn_3$ has the ordered Cu_3Au crystal structure.[14] The (nonrelativistic) Fermi level is at about − 0.5 Ry.[15]

Γ_{25}': $\vec{k} = (000)$. This representation allows La *d* and Sn *d* symmetry (Sn *d* on two of the three Sn sites making up the primitive cell). The La 5*d* is a valence electron at about − 0.45 Ry in the free La atom,[11] whereas Sn 4*d* lies roughly at − 2.5 Ry in the free Sn atom.[11] La 3*d* and 4*d* are at about − 63.7 and − 8.75 Ry, respectively.[11] Sn 3*d* is at about − 37.2 Ry.[11]

Table IV lists energy levels for five choices of calculation. MOPW orthogonalizes to La 3*d* and 4*d* and to Sn 3*d* and keeps La 5*d* and Sn 4*d*. OPW1 orthogonalizes to La 3*d*, 4*d*, and 5*d* and to Sn 3*d* and 4*d*. OPW2 orthogonalizes to La 3*d* and 4*d* and to Sn 3*d* and 4*d* and ignores La 5*d*. OPW3 orthogonalizes to La 3*d* and 4*d* and to Sn 3*d* and ignores La 5*d* and Sn 4*d*.

From Table IV we see that MOPW and MPW are virtually identical. This, plus the fact that the orthogonalized plane waves do contribute importantly to this level, indicates that La 3*d* and 4*d* and Sn 3*d* are accurate eigenfunctions for the crystal. Orthogonalizing to La 5*d* is not a good procedure (OPW1). Ignoring La 5*d* and treating Sn 4*d* as a lower atomic function, i.e., orthogonalizing to it (OPW2) agrees with MPW within about 0.02 Ry at 25 symmetrized plane waves. Ignoring both La 5*d* and Sn 4*d* (OPW3) produces very slow convergence. A comparison of Tables II and IV (OPW2 of each Table) indicates that ignoring the valence La 5*d* function in $LaSn_3$ produces much better results than ignoring the 3*d* function in Cu. This is very likely due to the presence of the lower-lying La and Sn *d*-type atomic functions in the $LaSn_3$ case.

Γ_{15}: $\vec{k} = (000)$. This representation allows La *p* symmetry and Sn *p* symmetry on two Sn sites. Sn 5*p* is a valence function at about − 0.44 Ry in the free atom.[11] La 5*p* lies roughly at − 1.94 Ry in the free atom.[11] La 2*p*, 3*p*, and 4*p* are at about − 403.0, − 82.2, and − 15.3 Ry, respectively.[11] Sn 2*p*, 3*p*, and 4*p* are at about −288.8, − 52.1, and − 7.06 Ry, respectively.[11]

Table V lists energy levels for five choices of calculation. Note that there are two levels for each truncation. MOPW orthogonalizes to La 2*p*, 3*p*, and 4*p* and to Sn 2*p*, 3*p*, and 4*p* and keeps La 5*p* and Sn 5*p*. OPW1 orthogonalizes to La 2*p*, 3*p*, 4*p*, and 5*p* and to Sn 2*p*, 3*p*, 4*p*, and 5*p*. OPW2 orthogonalizes to La 2*p*, 3*p*, 4*p*, and 5*p* and to Sn 2*p*, 3*p*, and 4*p* and ignores Sn 5*p*. OPW3 orthogonalizes to La 2*p*, 3*p*, and 4*p* and to Sn 2*p*, 3*p*, and 4*p* and ignores La 5*p* and Sn 5*p*.

As expected, MOPW gives levels practically identical to MPW. Including the two Sn 5*p* functions with the functions to which one orthogonalizes is not a good procedure (OPW1). Ignoring the two Sn 5*p* functions and orthogonalizing to the (marginally accurate) La 5*p* function (OPW2) gives results in fairly good agreement with MPW. Ignoring both the La 5*p* and the two Sn 5*p* functions (OPW3) converges quite rapidly and is in excellent agreement with MPW at 27 symmetrized plane waves.

Comparison of OPW3 of Table V with OPW3 of

TABLE IV. $\Gamma_{25'}$ energy levels for $LaSn_3$. All energies are in Ry.

Symmetrized plane waves	Magnitude squared	MPW	MOPW	OPW1	OPW2	OPW3
3	5	−0.4444	−0.4444		−0.1692	
13	13	−0.4510	−0.4509	0.0474	−0.3701	0.3770
25	20	−0.4576	−0.4575	0.0439	−0.4416	−0.0289
40	27	−0.4725	−0.4724		−0.4675	−0.2280

TABLE V. Γ_{15} energy levels for $LaSn_3$. All energies are in Ry.

Symmetrized plane waves	Magnitude squared	MPW	MOPW	OPW1	OPW2	OPW3
6	5	−0.0955	−0.0957	0.585	−0.0779	−0.0142
		−0.6310	−0.6314	0.215	−0.6046	−0.5571
16	11	−0.1069	−0.1071	0.530	−0.1223	−0.0902
		−0.6397	−0.6401	0.190	−0.6561	−0.6309
27	17	−0.1123	−0.1126	0.499	−0.1275	−0.1097
		−0.6425	−0.6428	0.179	−0.6588	−0.6407
39	22	−0.1144			−0.1290	−0.1135
		−0.6439			−0.6596	−0.6437

Table IV illustrates the fact that it generally takes far fewer plane waves to represent a p-type level than it does to represent a d-type level.

For $LaSn_3$ one might guess *a priori* that better results are obtained by orthogonalizing to the Sn 4d function than by ignoring it (OPW2 versus OPW3 of Table IV) whereas one does better by ignoring La 5p than by orthogonalizing to it (OPW3 versus OPW2 of Table V). One would guess this both from the generally more rapid convergence of p levels as opposed to d levels and from the following consideration: When the Herman-Skillman[11] free-atom functions are truncated by re-solving the Schrödinger equation with the muffin-tin restrictions as described earlier, somewhat higher energies result. Table VI shows that this truncation affected the Sn 4d atomic function much less than the La 5p atomic function, indicating that the truncated Sn 4d function is probably a better crystal eigenfunction than the truncated La 5p function.

IV. CONCLUSIONS

When standard OPW is applied to $LaSn_3$, electron energy levels in quite good agreement with MPW can be obtained by judiciously choosing whether to orthogonalize to a particular atomiclike function or to ignore it (see Tables IV and V). The MOPW method gives more rapid convergence to the MPW levels than OPW does, and whenever an atomic function is of doubtful accuracy as a crystal eigenfunction one simply keeps that function or an atomiclike function constructed from it as an explicit expansion function (in the form of a symmetrized Bloch sum).

Table VI. Change in La 5p and Sn 4d atomic energy levels due to the muffin-tin truncation. All energies are in Ry.

Function	Free-atom energy[a]	Truncated energy	Difference: Column 3 − Column 2
La 5p	−1.937	−1.824	0.113
Sn 4d	−2.526	−2.506	0.020

[a] From Ref. 11.

For Cu, standard OPW works quite well for a representation involving only p symmetry (see Table I). This would presumably also be the case for representations involving only s or only s and p symmetry. For representations involving d symmetry, however, we find MOPW to be far more suitable than OPW (see Tables II and III).

It should be appreciated that for Cu, with only a few atomic functions, there is no great advantage in using MOPW instead of MPW, but that for crystals with many atomic functions, such as $LaSn_3$, there can be considerable reduction in matrix size in going from MPW to MOPW, particularly at points of lower symmetry.

It could be argued that in going from OPW to MOPW, two additional types of integrals are introduced into the matrix formulation, namely, atomic-atomic and atomic plane-wave integrals. However, once programmed, this is of minor importance and it seems to us that these types of integrals are needed in forming the orthogonalized plane waves anyway.

We had originally hoped to give some general criteria which would enable one to tell *a priori* whether to orthogonalize to a given atomiclike function or to ignore it. The discussion associated with Table VI describes a possible criterion for atomiclike functions constructed as ours were. In a given calculation it is probably best to try the marginal functions both ways for one or two representations, although this can result in a considerable amount of computation. With the MOPW method this decision is not so crucial, since one can always "keep" the doubtful atomiclike functions at the expense of increasing the matrix size somewhat.

In summary, we feel that the basic OPW method, in the form of MOPW (or MPW when few atomic functions are involved) rather than in standard form, is actually a quite suitable method for crystals such as Cu. Standard OPW appears to be quite inadequate for Cu for those representations allowing *d* symmetry. For $LaSn_3$, although standard OPW would probably be suitable (particularly for a self-consistent treatment), MOPW converges more rapidly and more reliably.

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APPENDIX

In our version of MOPW, we approximate the true crystal wave function $\psi_t^n(\vec{r})$ by

$$\psi_a^n(\vec{r}) = \sum_i c_{ni}\,\phi_i(\vec{r}) \quad , \tag{A1}$$

where the ϕ_i are of two types: (i) higher atomiclike functions or cutoff functions (CO) and (ii) orthogonalized plane waves (OPW's). The variational procedure leads to the set of equations

$$\sum_j c_{nj} \int \phi_i^*(\vec{r})(H-E_n)\,\phi_j(\vec{r})\,d\tau = 0 \quad , \tag{A2}$$

where H is the Hamiltonian of the system and E_n is the energy eigenvalue. These equations are to be solved for each reciprocal space $\vec{k}$ value used. This set is equivalent to the matrix equation

$$\mathbf{H}\vec{c}_n = E_n \mathbf{S}\vec{c}_n \quad , \tag{A3}$$

where

$$H_{ij} = \int \phi_i^*(\vec{r})\,H\,\phi_j(\vec{r})\,d\tau \quad , \tag{A4}$$

$$S_{ij} = \int \phi_i^*(\vec{r})\,\phi_j(\vec{r})\,d\tau \quad . \tag{A5}$$

Since the ϕ_i are not necessarily orthogonal, $\mathbf{S}$ is not the identity matrix.

Schematically, the matrices are of the form

$$\mathbf{H} = \begin{pmatrix} (\mathrm{CO}|H|\mathrm{CO}) & (\mathrm{CO}|H|\mathrm{OPW}) \\ (\mathrm{OPW}|H|\mathrm{CO}) & (\mathrm{OPW}|H|\mathrm{OPW}) \end{pmatrix} . \tag{A6}$$

Define an orthogonalized plane wave as[16]

$$\phi(\vec{K}_i) = PW(\vec{K}_i) - \sum_b a_{ib}\,C_b(\vec{r}) \quad , \tag{A7}$$

with $PW(\vec{K}_i)$ being the ordinary plane-wave term and the $C_b(\vec{r})$ being the lower atomiclike functions. We write $\vec{K}_i$ for $\vec{k}_i + \vec{K}_i$. If the C_b satisfy

$$\langle C_b | C_t \rangle = \delta_{bt} \quad ,$$

then

$$a_{ib} = \langle C_b | \mathrm{PW}(\vec{K}_i) \rangle \quad . \tag{A8}$$

The OPW-OPW elements are

$$\langle \phi(\vec{K}_i) | H | \phi(\vec{K}_j) \rangle = \langle \mathrm{PW}(\vec{K}_i) | H | \mathrm{PW}(\vec{K}_j) \rangle - A - B + D \quad , \tag{A9}$$

where

$$A = \sum_b a_{ib}^* \langle C_b | H | \mathrm{PW}(\vec{K}_j) \rangle \quad ,$$

$$B = \sum_t a_{jt} \langle \mathrm{PW}(\vec{K}_i) | H | C_t \rangle \quad ,$$

$$D = \sum_{b,t} a_{ib}^* a_{jt} \langle C_b | H | C_t \rangle \quad .$$

If each C_b satisfies

$$HC_b(\vec{r}) = E_b C_b(\vec{r}) \quad , \tag{A10}$$

then Eq. (A9) reduces to

$$\langle \phi(\vec{K}_i) | H | \phi(\vec{K}_j) \rangle = \langle \mathrm{PW}(\vec{K}_i) | H | \mathrm{PW}(\vec{K}_j) \rangle - \sum_t a_{it}^* a_{jt} E_t \quad . \tag{A11}$$

In our application, some of our "lower" atomiclike functions do not satisfy (A10) exactly (because of fitting a cubic function onto them so that they go to zero with zero slope). We therefore used Eq. (A9) and not Eq. (A11). Calculation of the actual values indicated that taking $\langle C_b | H | C_t \rangle$ equal to zero for $b \neq t$ was still a good approximation. We further have

$$\langle \mathrm{PW}(\vec{K}_i) | H | \mathrm{PW}(\vec{K}_j) \rangle = (K_j^2 + \overline{V})\,(\mathrm{Vol})\,\delta_{ij} + 4\pi \times \int [V(r) - \overline{V}]\,j_0(Gr)\,r^2\,dr \quad , \tag{A12}$$

where $\overline{V}$ is the constant value of the potential between the muffin-tin spheres, Vol is the volume of the primitive cell, $\vec{G}$ is the reciprocal-lattice vector connecting $\vec{K}_i$ and $\vec{K}_j$, and j_0 is the spherical Bessel function of order zero. We have

$$\langle \phi(\vec{K}_i) | \phi(\vec{K}_j) \rangle = \langle \mathrm{PW}(\vec{K}_i) | \mathrm{PW}(\vec{K}_j) \rangle - \sum_t a_{it}^* a_{jt} \quad , \tag{A13}$$

$$\langle \mathrm{PW}(\vec{K}_i) | \mathrm{PW}(\vec{K}_j) \rangle = (\mathrm{Vol})\,\delta_{ij} \quad ; \tag{A14}$$

$$\begin{aligned} a_{jt} &= \langle C_t | \mathrm{PW}(\vec{K}_j) \rangle \quad , \qquad \text{see Eq. (A8)} \\ &= 4\pi X_t(\vec{K}_j) \int u_t(r)\,j_{l(t)}(K_j r)\,r\,dr \quad , \end{aligned} \tag{A15}$$

where $u_t(r) = u_{n(t)\,l(t)}(r)$ and $X_t(\vec{K}_j) = X_{l(t)q(t)}(\vec{K}_j)$ is a cubic harmonic which may be written as

$$X_{lq}(\theta, \phi) = \sum_m g_m^{lq}\,Y_{lm}(\theta, \phi) \quad ,$$

where the Y_{lm} are spherical harmonics. Equation (A15) is also valid for the $\langle \mathrm{CO} | \mathrm{PW}(\vec{K}_i) \rangle$ terms.

The CO-OPW elements are

$$\langle \mathrm{CO}_i | H | \phi(\vec{K}_j) \rangle = \langle \mathrm{CO}_i | H | \mathrm{PW}(\vec{K}_j) \rangle - \sum_t a_{jt} \langle \mathrm{CO}_i | H | C_t \rangle \quad . \tag{A16}$$

The CO functions could be explicitly orthogonalized to the C_t as was done by Deegan and Twose.[7] Our method of constructing the CO makes $\langle \mathrm{CO}_i | H | C_t \rangle$ automatically equal to zero for $l(i) \neq l(t)$, and actual calculation indicated that these terms are negligible for $n(i) \neq n(t)$ even when $l(i) = l(t)$. We have

$$\langle \mathrm{CO}_i | H | \mathrm{PW}(\vec{\mathrm{K}}_j) \rangle = K_j^2 \langle \mathrm{CO}_i | \mathrm{PW}(\vec{\mathrm{K}}_j) \rangle + 4\pi X_i(\vec{\mathrm{K}}_j) F_i(K_j) \tag{A17a}$$

with

$$F_i(K_j) = \int u_i(r) j_{l(i)}(K_j r) r V(r)\, dr \ . \tag{A17b}$$

Equation (A17a) is also used for those C_t which do not satisfy Eq. (A10) exactly. We also have

$$\langle \mathrm{CO}_i | \phi(\vec{\mathrm{K}}_j) \rangle = \langle \mathrm{CO}_i | \mathrm{PW}(\vec{\mathrm{K}}_j) \rangle - \textstyle\sum_t a_{jt} \langle \mathrm{CO}_i | C_t \rangle \ . \tag{A18}$$

As in Eq. (A16), we took the $\sum_t$ above to be zero.

The CO-CO elements are

$$\langle \mathrm{CO}_i | \mathrm{CO}_j \rangle = M_i \int u_i(r) u_j(r)\, dr\, \Delta_{ij} \ , \tag{A19}$$

with $M_i = \int X_i^2\,(\theta, \phi)\, d\Omega$, (A19′)

$$\Delta_{ij} = \delta_{l(i),l(j)} \delta_{q(i),q(j)} \quad . \tag{A19″}$$

$$\langle \mathrm{CO}_i | H | \mathrm{CO}_j \rangle = M_i \int u_i(r) H_r u_j(r)\, dr\, \Delta_{ij} \ , \tag{A20}$$

with M_i and Δ_{ij} as defined above and

$$H_r = -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) \ . \tag{A21}$$

Once the $\mathbf{S}$ and $\mathbf{H}$ matrix elements have been formed as indicated above, a unitary transformation which diagonalizes $\mathbf{S}$ is applied to Eq. (A3). This diagonalization utilizes the Jacobi routine.[17] Then Eq. (A3) becomes

$$\mathbf{H}' \vec{c}_n' = E_n \mathbf{S}_d \vec{c}_n' \ , \tag{A22}$$

with $\mathbf{H}' = \mathbf{U}^{-1} \quad \mathbf{U}$, $\vec{c}_n' = \mathbf{U}^{-1} \vec{c}_n$, and $\mathbf{S}_d = \mathbf{U}^{-1} \mathbf{S} \mathbf{U}$, a diagonal matrix. Equation (A22) can be written as

$$\mathbf{H}'' \vec{c}_n'' = E_n \vec{c}_n'' \ , \tag{A23}$$

where $\mathbf{H}''$ is the Hermitian matrix $\mathbf{S}_d^{-1/2} \mathbf{H}' \mathbf{S}_d^{-1/2}$ and $\vec{c}_n'' = \mathbf{S}_d^{1/2} \vec{c}_n'$. The Jacobi routine is applied again giving both the eigenvalues E_n and the eigenfunctions $\vec{c}_n''$. The original $\vec{c}_n$ are given by

$$\vec{c}_n = \mathbf{U} \mathbf{S}_d^{-1/2} \vec{c}_n'' \ . \tag{A24}$$

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[17] The Jacobi diagonalization program used here was written by F. W. Quelle.