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A Simulation of the Exchange Potential in Unrestricted and Restricted Hartree–Fock Calculations Studied on Atoms*

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The spherical average of the Hartree–Fock exchange potential depending on each spin orbital is compared with Slater's exchange potential, V_{XS}, as demonstrated for the phosphorus atom. It is shown that the former potential can be simulated by $(a + br)V_{XS}$, where r is the radius and the constants a and b are calculated for each spin orbital. This simulation is tested for the iron atom and it is found that the results agree well with those obtained from unrestricted and restricted Hartree–Fock calculations, respectively. The applicability of this new method in energy band structure calculations is briefly discussed.

Key words: Hartree–Fock exchange, simulation of ~ in atoms

1. Introduction

The calculation of the Hartree–Fock (HF) exchange potential in complicated systems such as crystals involves substantial computational effort. This is one of the reasons why "local potentials" based on the $\rho^{1/3}$ approximation, e.g. the Slater [1], the Gáspár–Kohn–Sham [2, 3], and the Xα [4] exchange potentials are widely used in energy band structure calculations. Slater's original intention was to simplify the HF equations. But later it was found [5] that local potential schemes based on the "density functional formalism" require an interpretation of the one-electron energies, which is different from the HF case.

In the present paper, a simulation of the HF exchange potential is proposed, which on the one hand keeps the simplicity of the $\rho^{1/3}$ potentials and thus allows an application in energy band structure calculations and on the other hand retains the main features of the HF method and the interpretation of the one-electron energies

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* Dedicated to Professor H. Hartmann on the occasion of his 65th birthday.

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according to Koopmans' theorem [6]. This new HF simulation method will be studied on atoms in order to check its applicability.

First, for illustration purposes, the HF exchange potentials for all orbitals of the phosphorus atom are compared with the orbital-independent Slater exchange potential. Then, the simulation procedure is outlined for the P-3p orbital.

Second, the iron atom is chosen as a test case for the accuracy of the present HF simulation, with the main emphasis on the one-electron energies.

2. The Spherical Average of the HF Exchange Potential

The HF equation for the spin orbital u_i can be written in the form [7]

$$[-\nabla_1^2 + V_{\mathrm{C}}(1) + V_{\mathrm{X}i}(1)]u_i(1) = \varepsilon_i u_i(1), \tag{1}$$

where V_{C} is the Coulomb potential and $V_{\mathrm{X}i}$, the exchange potential, given by

$$V_{\mathrm{X}i}(1) = -\sum_j w_j \left[\int u_i^*(1) u_j^*(2)(2/r_{12}) u_j(1) u_i(2)\, d\tau_2 \right] \Big/ [u_i^*(1) u_i(1)] \tag{2}$$

(using Rydberg atomic units), where $d\tau$ denotes integration over space variables and summation over the spins and w_j is the occupation number of the spin orbital u_j. We assume

$$u_i(1) = \varphi_i(1) \times \begin{cases} \alpha(m_{si}), & m_{si} = 1/2 \\ \beta(m_{si}), & m_{si} = -1/2 \end{cases} \tag{3}$$

with

$$\varphi_i(1) = R_{n_i l_i}(r_1) Y_{l_i m_i}(\Omega_1), \tag{4}$$

$R_{n_i l_i}(r)$ being the solution of the radial Schrödinger equation and $Y_{l_i m_i}(\Omega)$ a spherical harmonic.

If we calculate the spherical average of (2) for the spin up ($\uparrow$) orientation, $\bar{V}_{\mathrm{X}i\uparrow}(r_1)$, we obtain

$$\bar{V}_{\mathrm{X}i\uparrow}(r_1) = -\frac{1}{4\pi} \int_{\Omega_1} \left[\sum_{j\uparrow} w_j I_{ij} \right] \Big/ [\varphi_i^*(1) \varphi_i(1)]\, d\Omega_1, \tag{5}$$

$$I_{ij} = \int \varphi_i^*(1) \varphi_j^*(2)(2/r_{12}) \varphi_j(1) \varphi_i(2)\, dv_2, \tag{6}$$

where dv means integration over space variables only. We can solve the integral (6) by expanding $1/r_{12}$ in spherical harmonics [8]. Finally we obtain

$$\begin{aligned} \bar{V}_{\mathrm{X}i\uparrow}(r_1) &= \bar{V}_{\mathrm{X}n_i l_i m_i\uparrow}(r_1) \\ &= -[2/P_{n_i l_i}(r_1)] \sum_{n_j=1}^{n} \sum_{l_j=0}^{n_j-1} P_{n_j l_j}(r_1) \sum_{l=0}^{l_i+l_j} [1(2l+1)] \\ &\quad \cdot R_{l_j l_i l}^{n_j n_i}(r_1) \sum_{m_j=-l_j}^{l_j} w_{n_j l_j m_j \uparrow}\, Y_{l_j l_i l}^{m_j m_i m} \end{aligned} \tag{7}$$

with the following definitions:

$$P_{n_il_i}(r) = rR_{n_il_i}(r), \tag{8}$$

$$R^{n_jn_i}_{l_jl_il}(r_1) = (1/r_1^{l+1}) \int_0^{r_1} P_{n_il_i}(r)P_{n_jl_j}(r)r^l\,dr + r_1^l \int_{r_1}^{\infty} P_{n_il_i}(r)P_{n_jl_j}(r)(1/r^{l+1})\,dr, \tag{9}$$

$$Y^{m_jm_im}_{l_jl_il} = A^{m_jm_im}_{l_jl_il} \times C^{m_jm_im}_{l_jl_il}, \tag{10}$$

$$A^{m_jm_im}_{l_jl_il} = \int Y_{l_jm_j}(Y_{l_im_i})^{-1} Y^*_{lm}\,d\Omega, \tag{11}$$

$$C^{m_jm_im}_{l_jl_il} = \int Y^*_{l_jm_j} Y_{l_im_i} Y_{lm}\,d\Omega. \tag{12}$$

For closed-shell systems, (7) can be simplified to

$$\overline{V}_{\mathrm{X}n_il_i\uparrow}(r_1) = [1/(2l_i+1)] \sum_{m_i=-l_i}^{l_i} \overline{V}_{\mathrm{X}n_il_im_i\uparrow}(r_1) \tag{13}$$

by eliminating the dependence on m_i and by using the relation (Herzig [9], which is derived in the Appendix),

$$\sum_{m_i=-l_i}^{l_i} \sum_{m_j=-l_j}^{l_j} \sum_{m=-l}^{l} Y^{m_jm_im}_{l_jl_il} = (2l_i+1)(2l_j+1)(2l+1)\begin{pmatrix} l_i & l_j & l \\ 0 & 0 & 0 \end{pmatrix}^2, \tag{14}$$

where $\begin{pmatrix} l_i & l_j & l \\ 0 & 0 & 0 \end{pmatrix}$ are the Wigner 3-j coefficients for $m_i = m_j = m = 0$. Finally we obtain the following form (for both spin directions)

$$\overline{V}_{\mathrm{X}n_il_i}(r_1) = -[2/P_{n_il_i}(r_1)] \sum_{n_j=1}^{n} \sum_{l_j=0}^{n_j-1} (2l_j+1)P_{n_jl_j}(r_1) \cdot \sum_{l=0}^{l_i+l_j} \begin{pmatrix} l_i & l_j & l \\ 0 & 0 & 0 \end{pmatrix}^2 R^{n_jn_i}_{l_jl_il}(r_1). \tag{15}$$

3. Comparison between the HF and Slater's Exchange Potentials

In Figs. 1*a* and 1*b* the HF exchange potentials (according to Eq. 7) are shown for the orbitals of the phosphorus atom in its ground state. For the calculation of (9) the radial functions are taken from Clementi and Roetti [10]. (Figs. 1*a* and 1*b* are similar to results given by D. R. Hartree [11] for the closed shell system Cu^+, though he did not indicate the method of calculation.) One can see from these figures that in general the exchange potential decreases with increasing quantum numbers *n* and *l*. In its ground state ^4S, the phosphorus atom has 9 electrons with spin up (↑) and 6 with spin down (↓). Therefore the exchange potential for given quantum numbers *n* and *l* differs for spin up and spin down, where the modulus of the exchange potential of $nl\uparrow$ is always greater than that of $nl\downarrow$. It can also be seen

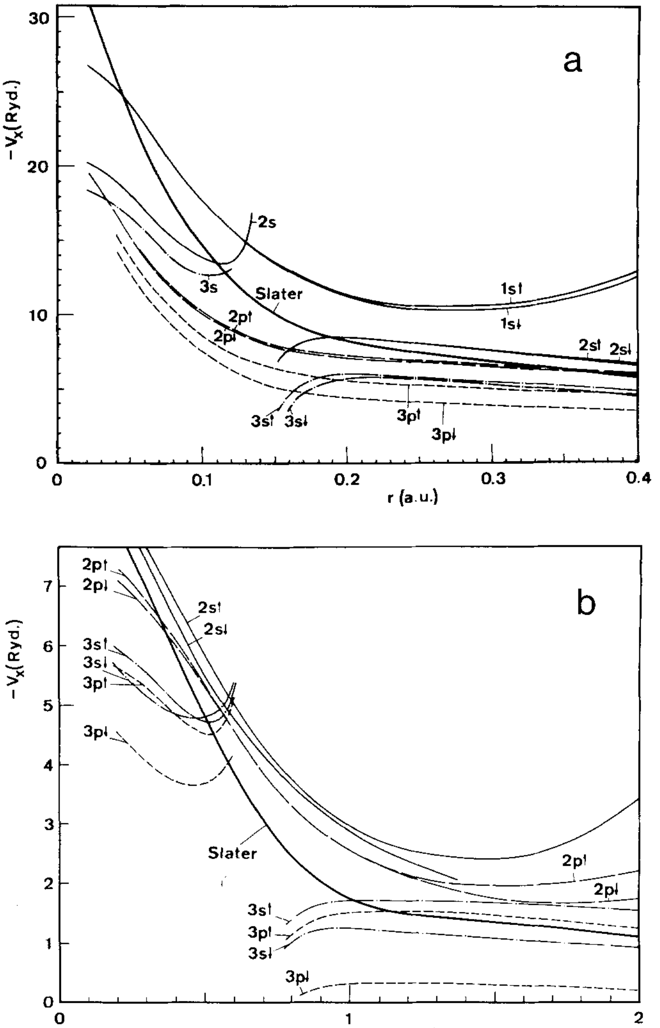

Fig. 1. Hartree–Fock (labelled by the orbital quantum numbers) and Slater's exchange potential versus the radius according to Eq. (7) and (16) for the phosphorus atom in its ground state ^4S

that the modulus of the exchange potential of the empty $3p\downarrow$ is considerably smaller than that of the occupied orbitals.

In Figs. 1*a* and *b* also Slater's exchange potential [1]

$$V_{XS}(r) = -3[(3/\pi)\rho(r)]^{1/3} \tag{16}$$

is given for comparison and shows that the Slater approximation overestimates the HF exchange potential in the region of small radii and underestimates the HF exchange in the region far away from the nucleus.

4. Method of Simulation

The HF exchange potential has the following features: 1) the dependence on the quantum numbers n, l, and m, 2) the dependence on the spin densities, and 3) the distinction between occupied and empty orbitals. Retaining these features, a simulation of the HF exchange potential of the form

$$V_{\mathrm{X}i\uparrow}(r) \approx (a_{i\uparrow} + b_{i\uparrow} r) V_{\mathrm{XS}}(r) \tag{17}$$

is proposed (analogously for the spin down case). This approximation is justified by the following consideration illustrated by an example:

In Fig. 2 a plot of the function

$$\tilde{\alpha}_{i\uparrow}(r) = V_{\mathrm{X}i\uparrow}(r)/V_{\mathrm{XS}}(r) \tag{18}$$

is shown together with the radial density

$$\sigma_i(r) = 4\pi r^2 R^2_{n_i l_i}(r) \tag{19}$$

for the $3p\uparrow$ orbital of the phosphorus atom in its ground state ^4S. It can be seen from this figure that $\tilde{\alpha}$ is almost linear in the region of high density σ, where the approximation should be accurate, a fact, which justifies ansatz (17). In order to have a unique procedure for the determination of the a and b values we take the tangent to $\tilde{\alpha}_i$ at that radius, where σ_i has its absolute maximum.

5. Results

The calculation of the spherical averaged HF exchange potential is a straightforward procedure once the angular dependent integrals (10) are evaluated. In all calculations discussed here the required integrals (11) can be obtained analytically. However, for the general case a closed formula for evaluating (11) is unknown to the author.

A simulation of the HF exchange potential as described in the previous section was

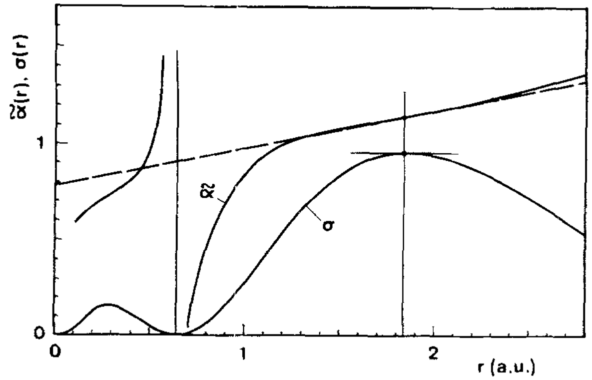

Fig. 2. For the $3p\uparrow$-orbital of the phosphorus atom in its ground state ^4S the following two quantities are shown as a function of the radius, r: (1) the function $\tilde{\alpha}$ (dimensionless) defined by Eq. (18), and (2) the radial charge density σ (in atomic units) according to Eq. (19)

Table 1. Values of *a* and *b* parameters for the iron atom, Fe $1s^2 2s^2 2p^6 3s^2 3p^6 (3d\uparrow)^5 (3d\downarrow)^1 4s^2$, in its ground state ^5D. *w* denotes the occupation number of the orbital with quantum numbers *n*, *l*, and *m* and spin up (↑) or spin down (↓)

nlm	*w*	*a*	*b*	*nlm*	*w*	*a*	*b*
100	↑ 1	0.90490	5.95954	31−1	↓ 1	0.68924	0.37829
100	↓ 1	0.90491	5.95917	310	↓ 1	0.64660	0.33652
200	↑ 1	0.89148	1.21974	311	↓ 1	0.64660	0.33652
200	↓ 1	0.91698	1.05409	32−2	↑ 1	0.67522	0.42598
21−1	↑ 1	0.76701	1.40091	32−1	↑ 1	0.67522	0.42598
210	↑ 1	0.76701	1.40091	320	↑ 1	0.67522	0.42598
211	↑ 1	0.76701	1.40091	321	↑ 1	0.67522	0.42598
21−1	↓ 1	0.77916	1.30256	322	↑ 1	0.67522	0.42598
210	↓ 1	0.78379	1.26185	32−2	↓ 1	0.61808	0.32944
211	↓ 1	0.78379	1.26185	32−1	↓ 0	0.28449	0.15112
300	↑ 1	0.81349	0.57807	320	↓ 0	0.28344	0.14987
300	↓ 1	0.73496	0.43179	321	↓ 0	0.27128	0.13553
31−1	↑ 1	0.77855	0.51117	322	↓ 0	0.27128	0.13553
310	↑ 1	0.77855	0.51117	400	↑ 1	0.57238	0.16948
311	↑ 1	0.77855	0.51117	400	↓ 1	0.33272	0.23772

performed for the iron atom in its ground state ^5D and led to *a* and *b* parameters for each spin orbital as given in Table 1, where for the evaluation of (9) the radial wave functions from Clementi and Roetti [10] have been used. It can be seen from Table 1 that the values of *a* and *b* generally decrease with increasing quantum numbers *n* and *l* and that they differ markedly between the occupied and unoccupied 3*d*-states. In addition, the *a* and *b* values corresponding to orbitals with the same *n*, *l*, and *m* quantum numbers but opposite spin are affected by the unsymmetrical spin distribution of the *d*-electrons.

Using the *a* and *b* values from Table 1, an exchange potential for each orbital is defined by Eq. (17). With these potentials a self-consistent atomic calculation can be carried out using a modified Herman–Skillman program [12]. The iteration procedure can be started by using $X\alpha_{vt}$ [13] wave functions to generate the first V_{XS} needed in Eq. (17).

Averaging the *a* and *b* values only over the quantum number *m* we obtain an exchange potential that depends on the quantum numbers *n* and *l* and on the spin direction. The method using these *a* and *b* values will be called "spin-polarized simulated Hartree–Fock" (SP-SHF) method, which simulates unrestricted HF calculations. Averaging the *a* and *b* values also over both spin directions, a *nl*-dependent exchange potential is obtained and the method employing these parameters will be termed "simulated Hartree–Fock" (SHF) method, which should be compared with restricted HF calculations. If the SHF parameters are calculated for a number of different atoms (as was actually done for the atoms He to Zn) the *Z*-dependence of the *a* and *b* values can be approximated by the equations

$$a_{nl}(Z) = A_{nl} + A'_{nl}Z, \tag{20}$$

$$b_{nl}(Z) = B_{nl} + B'_{nl}Z, \tag{21}$$

Table 2. One-electron energies (in Ryd) of the iron atom, Fe $1s^22s^22p^63s^23p^6(3d\uparrow)^5(3d\downarrow)^14s^2$ in its ground state ^5D

	SP-SHF	SHF	ASHF	RHF	UHF	HFS
$1s\uparrow$	−523.4170	−523.4122	−523.7161	−522.7472	−522.7489	−515.7652
$1s\downarrow$	−523.4176				−522.7497	
$2s\uparrow$	−63.8864	−63.8274	−64.0376	−63.8717	−63.9986	−60.9018
$2s\downarrow$	−63.7781				−63.7529	
$2p\uparrow$	−54.9161	−54.8573	−54.9326	−54.8280	−54.9506	−53.0300
$2p\downarrow$	−54.8082				−54.7133	
$3s\uparrow$	−8.6353	−8.2658	−8.3759	−8.3389	−8.3389	−7.2108
$3s\downarrow$	−7.9046				−7.9881	
$3p\uparrow$	−5.9292	−5.4706	−5.5863	−5.4843	−5.9166	−4.8330
$3p\downarrow$	−5.0731				−5.0591	
$3d\uparrow$	−1.4654	−1.3908	−1.2482	−1.2938	−1.3761	−8.9060
$3d\downarrow$	−1.0430				−0.9374	
$4s\uparrow$	−0.5342	−0.4991	−0.5282	−0.5163	−0.5544	−0.4775
$4s\downarrow$	−0.4708				−0.4844	

SP-SHF	spin polarized simulated Hartree-Fock
SHF	simulated Hartree-Fock
ASHF	averaged simulated Hartree-Fock
RHF	restricted Hartree-Fock [10]
UHF	unrestricted Hartree-Fock [16]
HFS	Hartree-Fock-Slater

where the values of A, A', B, and B' are listed in Table 3. This kind of approximation will be called "averaged simulated Hartree–Fock" (ASHF) method.

The one-electron energies of the iron atom in its ground state obtained by the three simulation methods described above are given in Table 2, which also contains the corresponding HF results and the Hartree–Fock–Slater (HFS) one-electron energies using Slater's exchange potential.

Table 3. Values for ASHF as defined in Eqs. (20) and (21)

	A	A'	B	B'
$1s$	0.86349	0.00168	0.07355	0.22703
$2s$	0.79733	0.00403	0.00231	0.04415
$2p$	0.76212	0.00003	−0.08952	0.05497
$3s$	0.85025	−0.00310	−0.24691	0.02915
$3p$	0.73488	−0.00058	−0.20588	0.02458
$3d$	0.63462	−0.00159	−0.22931	0.02449
$4s$	1.55562	−0.04228	−0.25650	0.01815

6. Discussion

The one-electron energies for the iron atom (Table 2) show that the simulation methods proposed here reproduce the corresponding HF results quite well considering the simplicity of the simulations, where the SP-SHF results should be compared with unrestricted HF (UHF) results, and the SHF and ASHF methods correspond to the restricted HF (RHF) method. Relatively large deviations are found for the $3d$ electrons for which the SP-SHF and SHF methods overestimate the HF exchange potential.

The overall good agreement between the one-electron energies obtained with the SHF and RHF methods remains about the same if the SHF method is replaced by the much simpler ASHF approximation (Table 2), where the a and b parameters required can easily be obtained for every atom (He–Zn) from Eqs. (20) and (21) using Table 3.

The direct comparison between the HFS and HF results is complicated by the fact [4, 5, 14] that the one-electron energies in the HF method and in the local potential schemes are interpreted differently. Therefore the HFS values differ markedly from all other results listed in Table 2.

Considering the wave functions it is found that the HF, the simulated HF, and the $X\alpha_{vt}$ results are very similar, but all of them deviate considerably from the HFS wave functions. This deviation of the HFS wave functions from the HF results has already been discussed [4].

In contrast to the local potential schemes, where the exchange (and correlation) potential is orbital independent, different potentials for different orbitals are used in a SHF calculation and therefore the SHF wave functions are not necessarily orthogonal to each other. However, since the SHF orbitals are very similar to HF orbitals, which are orthogonal, the non-orthogonality of the SHF wave functions should be of minor importance.

7. Conclusions

It is possible to simulate unrestricted and restricted HF calculations on atoms by replacing the exchange term in the HF one-electron equations for each orbital by a linear radial dependent form involving Slater's exchange approximation. With this new simulation both the HF one-electron energies and the HF wave functions can be reproduced accurately considering the simplicity of the simulation, particularly that of the ASHF method.

The proposed HF simulation method could be carried over to energy band structure calculations on solids. The necessary a and b parameters could be taken from the free atoms, if the electrons in the solid are fairly well localized and if it is obvious which bands will be occupied in the solid. This last restriction comes about since the HF (and thus also the SHF) exchange potentials differ substantially between occupied and unoccupied levels. Ionic insulators are a type of solid where these requirements are satisfied and hence the suggested simulation could be useful.

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Appendix

The derivation of Eq. (14) given here is due to Herzig [9]. The phase convention of Condon and Shortly is used for the spherical harmonics.
Consider

$$A_{l_j l_i l}^{m_j m_i m} = \int Y_{l_j m_j}(Y_{l_i m_i})^{-1} Y^*_{lm}\,d\Omega = (-1)^m \int Y_{l_j m_j}(Y_{l_i m_i})^{-1} Y_{l,-m}\,d\Omega.$$

Then the product of the two spherical harmonics in the numerator of the integral can be written as a linear combination of spherical harmonics (Edmonds [15], eq. (4.6.5)),

$$A_{l_j l_i l}^{m_j m_i m} = (-1)^m \sum_{LM} [(2l_j + 1)(2l + 1)(2L + 1)/(4\pi)]^{1/2}$$
$$\cdot \begin{pmatrix} l_j & l & L \\ m_j & -m & M \end{pmatrix} \begin{pmatrix} l_j & l & L \\ 0 & 0 & 0 \end{pmatrix} \int Y^*_{LM}(Y_{l_i m_i})^{-1}\,d\Omega,$$

and with

$$Y^*_{LM} = (-1)^M Y_{L,-M},$$
$$(-1)^{m+M} = (-1)^{m_j},$$

then

$$A_{l_j l_i l}^{m_j m_i m} = (-1)^{m_j} \sum_{LM} [(2l_j + 1)(2l + 1)(2L + 1)/(4\pi)]^{1/2}$$
$$\cdot \begin{pmatrix} l_j & l & L \\ m_j & -m & M \end{pmatrix} \begin{pmatrix} l_j & l & L \\ 0 & 0 & 0 \end{pmatrix} \int Y_{L,-M}(Y_{l_i m_i})^{-1}\,d\Omega.$$

Define the coefficients $C_{l_j l_i l}^{m_j m_i m}$, which can be expressed in terms of the 3-*j* coefficients using [15], eq. (4.6.3) as follows

$$C_{l_j l_i l}^{m_j m_i m} = \int Y^*_{l_j m_j} Y_{lm} Y_{l_i m_i}\,d\Omega = (-1)^{m_j} \int Y_{l_j,-m_j} Y_{lm} Y_{l_i m_i}\,d\Omega$$
$$= (-1)^{m_j}[(2l_j + 1)(2l + 1)(2l_i + 1)/(4\pi)]^{1/2} \begin{pmatrix} l_j & l & l_i \\ -m_j & m & m_i \end{pmatrix} \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix}.$$

It is

$$\begin{pmatrix} l_j & l & l_i \\ -m_j & m & m_i \end{pmatrix} = (-1)^{l_j + l + l_i} \begin{pmatrix} l_j & l & l_i \\ m_j & -m & -m_i \end{pmatrix}$$

([15], eq. (3.7.6)). Then

$$C_{l_j l_i l}^{m_j m_i m} = (-1)^{m_j}[(2l_j + 1)(2l + 1)(2l_i + 1)/(4\pi)]^{1/2}$$
$$\cdot \begin{pmatrix} l_j & l & l_i \\ m_j & -m & -m_i \end{pmatrix} \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix}$$

which vanishes if the sum $l_j + l + l_i$ is odd.

Combining the results and summing over m_j and m we have

$$\begin{aligned}\sum_{m_j m} Y_{l_j l_i l}^{m_j m_i m} &= \sum_{m_j m} A_{l_j l_i l}^{m_j m_i m} C_{l_j l_i l}^{m_j m_i m} \\ &= \sum_{LM} [(2l_j + 1)(2l + 1)/(4\pi)][(2L + 1)(2l_i + 1)]^{1/2} \\ &\quad \cdot \begin{pmatrix} l_j & l & L \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix} \sum_{m_j m} \begin{pmatrix} l_j & l & L \\ m_j & -m & M \end{pmatrix} \begin{pmatrix} l_j & l & l_i \\ m_j & -m & -m_i \end{pmatrix} \\ &\quad \cdot \int Y_{L,-M}(Y_{l_i m_i})^{-1}\, d\Omega.\end{aligned}$$

Applying the orthogonality relation of the 3-j coefficients ([15], eq. (3.7.8)) and using

$$\int Y_{l_i m_i}(Y_{l_i m_i})^{-1}\, d\Omega = 4\pi$$

we obtain the result

$$\sum_{m_j m} Y_{l_j l_i l}^{m_j m_i m} = (2l_j + 1)(2l + 1) \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix}^2 .$$

Since this sum is independent of m_i a summation over m_i gives only a factor of $(2l_i + 1)$, and we have finally

$$\sum_{m_i m_j m} Y_{l_j l_i l}^{m_j m_i m} = (2l_i + 1)(2l_j + 1)(2l + 1) \begin{pmatrix} l_j & l & l_i \\ 0 & 0 & 0 \end{pmatrix}^2 .$$

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