Decomposition of the two-electron-atom eigenvalue problem

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Following Bhatia and Temkin [Rev. Mod. Phys. **36**, 1050 (1964)] we decompose the Hamiltonian of a two-electron atom (or ion) with a fixed nucleus in terms of Euler angles, and thereby reduce the energy-eigenvalue problem to a set of coupled equations involving only three lengths, the distance of the electrons from each other and the distances from the nucleus. However, our equations differ from those of Bhatia and Temkin since we use a different expansion of the wave function. When the total orbital-angular-momentum quantum number L is zero or one our equations are the same as those derived by Hylleraas [Z. Phys. **48**, 469 (1928)] and Breit [Phys. Rev. **35**, 569 (1930)]. We give the transformation relating the generalized Hylleraas-Breit equations to the equations of Bhatia and Temkin. Our derivation is facilitated by a special factorization of one-particle angular-momentum operators.

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I. INTRODUCTION

Ignoring electron spin, a two-electron atom (or ion) with a fixed nucleus has six degrees of freedom, e.g., the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ which locate the electrons relative to the nucleus. The Hamiltonian of the system is (we use atomic units throughout)

$$H_a = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_3}, \tag{1}$$

where $\mathbf{r}_3 \equiv \mathbf{r}_1 - \mathbf{r}_2$ is the separation between the electrons. Since the Hamiltonian is invariant under a rotation, we may assume that an eigenfunction of the Hamiltonian is simultaneously an eigenfunction of the total orbital-angular-momentum operator $\mathbf{L}^2$ and its projection L_z along a fixed axis, say the z axis, with eigenvalues $L(L+1)$ and M, respectively. Eigenfunctions of $\mathbf{L}^2$ and L_z are finite linear combinations of the rotation matrices $\mathcal{D}_L^{M,K}(\alpha,\beta,\gamma)$, where the Euler angles α, β, and γ specify the orientation of a body-fixed Cartesian system (x',y',z') relative to a space-fixed system (x,y,z) (see, e.g., the book by Edmonds [1]). Here K is an eigenvalue of the projection of the total orbital angular momentum along the z' axis, and if Π $(=\pm 1)$ is the parity we have $\Pi = (-1)^K$. The complete eigenfunction $\Phi_\Pi^{L,M}(\mathbf{r}_1,\mathbf{r}_2)$ can therefore be expressed as the finite sum

$$\Phi_\Pi^{L,M}(\mathbf{r}_1,\mathbf{r}_2) = \sum_{K=-L,\,(-1)^K=\Pi}^{K=L} \mathcal{D}_L^{M,K}(\alpha,\beta,\gamma) f_K^L(r_1,r_2,r_3). \tag{2}$$

It follows that the energy-eigenvalue problem, i.e., $H_a|\Phi_\Pi^{L,M}\rangle = E|\Phi_\Pi^{L,M}\rangle$, can be reduced to a set of coupled differential equations for functions in the three variables r_1, r_2, and r_3.

A set of equations in these three variables was originally worked out for S states $(L=0)$ by Hylleraas [2], and later for P states $(L=1)$ by Breit [3]. [The equations of Breit were based on an expansion that is different from Eq. (2) — see below.] Subsequently, Bhatia and Temkin [4] gave a general derivation, applicable to arbitrary L. While the equations of Bhatia and Temkin are equivalent to those of Breit when $L=1$, the form of their equations is somewhat more complicated; see Appendix III of Ref. [4]. In this paper we generalize the Breit equations to all L by expanding $\Phi_\Pi^{L,M}(\mathbf{r}_1,\mathbf{r}_2)$ in terms of special linear combinations of the rotation matrices; this expansion coincides with Breit's expansion when $L=1$. Our derivation follows that of Bhatia and Temkin in so far as we make an Euler angle decomposition of the Hamiltonian, but by contrast we utilize a special factorization of one-particle angular-momentum operators which greatly facilitates our analysis. In the Appendix to this paper we give the (nontrivial) transformation relating our set of equations to those of Bhatia and Temkin. However, while we have chosen to decompose the Hamiltonian in Euler angles in order to make contact with Bhatia and Temkin, a simpler derivation of the generalized Breit equations can be given by expressing the Hamiltonian in Cartesian coordinates, as indicated at the end of this Introduction.

Choosing the z axis to be the polar axis, and defining θ_1 and ϕ_1 to be the polar and azimuthal angles of $\mathbf{r}_1$, and θ_2 and ϕ_2 to be the polar and azimuthal angles of $\mathbf{r}_2$, we introduce

$$\zeta_1 = \sin(\theta_1)e^{i\phi_1}, \tag{3}$$

$$\zeta_2 = \sin(\theta_2)e^{i\phi_2}. \tag{4}$$

Note that, with l_1 and l_2 non-negative integers, $L_z\zeta_1^{l_1}\zeta_2^{l_2} = (l_1+l_2)\zeta_1^{l_1}\zeta_2^{l_2}$. Furthermore, denoting the angular-momentum raising and lowering operators by L_+ and L_-, respectively, we have $L_+\zeta_1^{l_1}\zeta_2^{l_2} = 0$. It follows that $\zeta_1^{l_1}\zeta_2^{l_2}$ is an eigenfunction of both $\mathbf{L}^2$ and L_z, with eigenvalues $L(L+1)$ and L, respectively, where $L = l_1 + l_2$. There are $L+1$ possible (linearly independent) terms $\zeta_1^{l_1}\zeta_2^{l_2}$ for which $l_1+l_2=L$, and each term has parity $(-1)^L$. Since, for fixed L and M, there are $L+1$ linearly independent rotation matrices with parity $(-1)^L$, an eigenfunction of $\mathbf{L}^2$ and L_z with eigenvalues $L(L+1)$ and L, and with parity $(-1)^L$, is, in general, composed of all possible terms $\zeta_1^{l_1}\zeta_2^{l_2}$ for which $l_1+l_2=L$. Therefore, if $\Pi=(-1)^L$, we can expand an eigenfunction for which $M=L$ in the form

$$\Phi^{L,M=L}_{\Pi=(-1)^L}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{l_1+l_2=L} r_1^{l_1}r_2^{l_2}\zeta_1^{l_1}\zeta_2^{l_2}f^L_{l_1,l_2}(r_1,r_2,r_3). \tag{5}$$

To develop the corresponding expansion for the case $\Pi=-(-1)^L$, we restrict l_1 and l_2 to $l_1+l_2=L-1$, so that $\zeta_1^{l_1}\zeta_2^{l_2}$ has parity $-(-1)^L$ and is an eigenfunctions of $\mathbf{L}^2$ and L_z with eigenvalues $L(L-1)$ and $L-1$, and we multiply $\zeta_1^{l_1}\zeta_2^{l_2}$ by an angular function Θ which has positive parity and is such that $L_+\Theta=0$ and $L_z\Theta=\Theta$. The L linearly independent terms $\Theta\zeta_1^{l_1}\zeta_2^{l_2}$ are eigenfunctions of $\mathbf{L}^2$ and L_z, with eigenvalues $L(L+1)$ and L, and each term has parity $-(-1)^L$. Referring to the expressions for L_z and L_+ given by Eqs. (29) and (31) below, we see that a suitable choice for Θ is $\Theta=e^{i\alpha}\sin\beta$. Hence, noting that there are L linearly independent rotation matrices with parity $-(-1)^L$, we can expand an eigenfunction for which $M=L$ and $\Pi=-(-1)^L$ in the form

$$\Phi^{L,M=L}_{\Pi=-(-1)^L}(\mathbf{r}_1,\mathbf{r}_2)=e^{i\alpha}\sin(\beta)\,r_1r_2\sin(\theta_{12})\times\sum_{l_1+l_2=L-1} r_1^{l_1}r_2^{l_2}\zeta_1^{l_1}\zeta_2^{l_2}f^L_{l_1,l_2}(r_1,r_2,r_3), \tag{6}$$

where θ_{12} is the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$, and where we have introduced the factor $r_1r_2\sin\theta_{12}$ since its inclusion leads to the simplest form of the radial equations.

Eigenfunctions with total magnetic quantum number $M<L$ can be generated by application of L_-; the action of L_- on an eigenvector of $\mathbf{L}^2$ and L_z is straightforward to evaluate. Incidentally, if S is the total spin quantum number, the Pauli principle implies that $f^L_{l_1,l_2}(r_1,r_2,r_3)=(-)^{L+S}\Pi f^L_{l_2,l_1}(r_2,r_1,r_3)$.

The result of applying H_a to an S-state eigenfunction ($L=0=M$) was worked out many years ago and is[2]

$$H_a\Phi^{0,0}(\mathbf{r}_1,\mathbf{r}_2)=H_a^{(0)}f^0_{0,0}(r_1,r_2,r_3) \tag{7}$$

where $H_a^{(0)}$ is the differential operator

$$H_a^{(0)}\equiv-\frac{1}{2}\left[\frac{\partial^2}{\partial r_1^2}+\frac{2}{r_1}\frac{\partial}{\partial r_1}+\frac{\partial^2}{\partial r_2^2}+\frac{2}{r_2}\frac{\partial}{\partial r_2}+2\frac{\partial^2}{\partial r_3^2}+\frac{4}{r_3}\frac{\partial}{\partial r_3}+\left(\frac{r_1^2-r_2^2+r_3^2}{r_1r_3}\right)\frac{\partial^2}{\partial r_1\partial r_3}+\left(\frac{r_2^2-r_1^2+r_3^2}{r_2r_3}\right)\frac{\partial^2}{\partial r_2\partial r_3}\right]-\frac{Z}{r_1}-\frac{Z}{r_2}+\frac{1}{r_3}. \tag{8}$$

In this paper we show that, for all L, and parity $(-1)^L$,

$$H_a\Phi^{L,M=L}_{\Pi=(-1)^L}(\mathbf{r}_1,\mathbf{r}_2)=\sum_{l_1+l_2=L} r_1^{l_1}r_2^{l_2}\zeta_1^{l_1}\zeta_2^{l_2}q^L_{l_1,l_2}(r_1,r_2,r_3), \tag{9}$$

where, suppressing the arguments r_1, r_2, and r_3,

$$q^L_{l_1,l_2}=H_a^{(0)}f^L_{l_1,l_2}-\left(\frac{l_1}{r_1}\frac{\partial}{\partial r_1}+\frac{l_2}{r_2}\frac{\partial}{\partial r_2}+\frac{(l_1+l_2)}{r_3}\frac{\partial}{\partial r_3}\right)f^L_{l_1,l_2}+\left(\frac{l_1+1}{r_3}\right)\frac{\partial f^L_{l_1+1,l_2-1}}{\partial r_3}+\left(\frac{l_2+1}{r_3}\right)\frac{\partial f^L_{l_1-1,l_2+1}}{\partial r_3}, \tag{10}$$

while for parity $-(-1)^L$

$$H_a\Phi^{L,M=L}_{\Pi=-(-1)^L}(\mathbf{r}_1,\mathbf{r}_2)=e^{i\alpha}\sin(\beta)\,r_1r_2\sin(\theta_{12})\sum_{l_1+l_2=L-1} r_1^{l_1}r_2^{l_2}\zeta_1^{l_1}\zeta_2^{l_2}q^L_{l_1,l_2}(r_1,r_2,r_3), \tag{11}$$

where

$$q^L_{l_1,l_2}=H_a^{(0)}f^L_{l_1,l_2}-\left(\frac{(l_1+1)}{r_1}\frac{\partial}{\partial r_1}+\frac{(l_2+1)}{r_2}\frac{\partial}{\partial r_2}+\frac{(l_1+l_2+2)}{r_3}\frac{\partial}{\partial r_3}\right)f^L_{l_1,l_2}+\left(\frac{l_1+1}{r_3}\right)\frac{\partial f^L_{l_1+1,l_2-1}}{\partial r_3}+\left(\frac{l_2+1}{r_3}\right)\frac{\partial f^L_{l_1-1,l_2+1}}{\partial r_3}. \tag{12}$$

It is simple to extend Eqs. (9) and (11) to $M<L$ since the angular-momentum lowering operator L_- commutes with H_a. The eigenvalue problem $H_a|\Phi^{L,M}_\Pi\rangle=E|\Phi^{L,M}_\Pi\rangle$ gives rise to the M-independent coupled equations

$$q^L_{l_1,l_2}=Ef^L_{l_1,l_2}, \tag{13}$$

since each term on the right-hand sides of Eqs. (5), (6), (9), and (11) is linearly independent (for we may hold

r_1, r_2, and r_3 fixed while varying ζ_1). For $L = 1$ we recover the Breit equations [3]. Accurate calculations of atomic properties of helium have been performed by, for example, Kono and Hattori [5] and Drake [6], who used basis functions in the coordinates r_1, r_2, and r_3 [multiplied by vector-coupled spherical harmonics $\mathcal{Y}_{l_1 l_2}^{LM}$, which for $M = L$ are equivalent to our angular functions for the case $\Pi = (-1)^L$]. It is often more convenient to work with perimetric coordinates, which are special linear combinations of r_1, r_2, and r_3; see, e.g., Pekeris [7], or more recently Wintgen and Delande [8]. The relevant equations for the eigenvalue problem in perimetric coordinates may be obtained directly from Eqs. (13).

In the next section we discuss the Euler angles and in Sec. III we discuss the angular-momentum operators. While the material in these first two sections is not new, it is introduced as a preliminary to Sec. IV, where we describe the key development — the factorization of the one-particle angular-momentum operators in terms of derivatives with respect to the Euler angles and the angle θ_{12}. This factorization is an invaluable tool in simplifying the two-electron Laplacian, which is carried out in Sec. V.

We conclude this Introduction by returning to our earlier remark that the generalized Breit equations, i.e., Eqs. (13), can be derived without decomposing the Hamiltonian in Euler angles. We first recognize that the factor $(r_1\zeta_1)^{l_1}(r_2\zeta_2)^{l_2}$ in the expansion of Eq. (5) can be written as $(x_1 + iy_1)^{l_1}(x_2 + iy_2)^{l_2}$, which is a polynomial in Cartesian coordinates, and is in fact a solution of the Laplace equation. Therefore, the application of the Laplacian to the right-hand side of Eq. (5) can be carried out if the Laplacian is expressed in Cartesian coordinates (note r_1, r_2, and r_3 are simple functions of Cartesian coordinates). A similar statement holds for Eq. (6) upon recognizing (see the next section) that the factor $e^{i\alpha}\sin(\beta)\, r_1 r_2 \sin(\theta_{12})(r_1\zeta_1)^{l_1}(r_2\zeta_2)^{l_2}$ can be written as $-i[(x_1+iy_1)z_2-(x_2+iy_2)z_1](x_1+iy_1)^{l_1}(x_2+iy_2)^{l_2}$; again, this factor is a solution of the Laplace equation.

II. EULER ANGLES

Let the unit vectors $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ form a right-handed triad (i.e., $\hat{\mathbf{z}} = \hat{\mathbf{x}}\times\hat{\mathbf{y}}$) fixed in space. Let the unit vectors $\hat{\mathbf{x}}'$, $\hat{\mathbf{y}}'$, and $\hat{\mathbf{z}}'$ form a body-fixed right-handed triad, whose orientation relative to the space-fixed frame is specified by the standard Euler angles α, β, and γ (see, e.g., [1]):

$$\begin{aligned}\hat{\mathbf{x}}' &= (\cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma)\hat{\mathbf{x}}\\ &\quad+(\sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma)\hat{\mathbf{y}}\\ &\quad-(\sin\beta\cos\gamma)\hat{\mathbf{z}}, \end{aligned}\tag{14}$$

$$\begin{aligned}\hat{\mathbf{y}}' &= -(\cos\alpha\cos\beta\sin\gamma + \sin\alpha\cos\gamma)\hat{\mathbf{x}}\\ &\quad+(-\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma)\hat{\mathbf{y}}\\ &\quad+(\sin\beta\sin\gamma)\hat{\mathbf{z}}, \end{aligned}\tag{15}$$

$$\hat{\mathbf{z}}' = \cos\alpha\sin\beta\hat{\mathbf{x}} + \sin\alpha\sin\beta\hat{\mathbf{y}} + \cos\beta\hat{\mathbf{z}}, \tag{16}$$

with $0 \le \alpha < 2\pi$, $0 \le \beta \le \pi$, and $0 \le \gamma < 2\pi$. The "body" is the atom, whose electrons are located relative to the nucleus by the coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$. Hence, with θ_{12} the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$, we follow Bhatia and Temkin [4] (with a minor difference in the definition of the Euler angles — see the Appendix) and define the body-fixed triad as

$$\hat{\mathbf{x}}' = \frac{\hat{\mathbf{r}}_1 + \hat{\mathbf{r}}_2}{2\cos(\theta_{12}/2)}, \tag{17}$$

$$\hat{\mathbf{y}}' = \frac{\hat{\mathbf{r}}_2 - \hat{\mathbf{r}}_1}{2\sin(\theta_{12}/2)}, \tag{18}$$

$$\hat{\mathbf{z}}' = \frac{\hat{\mathbf{r}}_1 \times \hat{\mathbf{r}}_2}{\sin\theta_{12}}. \tag{19}$$

It follows that

$$\begin{aligned}\hat{\mathbf{r}}_1 &= [\cos\alpha\cos\beta\cos(\gamma - \tfrac{1}{2}\theta_{12}) - \sin\alpha\sin(\gamma - \tfrac{1}{2}\theta_{12})]\hat{\mathbf{x}}\\ &\quad+[\sin\alpha\cos\beta\cos(\gamma - \tfrac{1}{2}\theta_{12}) + \cos\alpha\sin(\gamma - \tfrac{1}{2}\theta_{12})]\hat{\mathbf{y}}\\ &\quad-\sin\beta\cos(\gamma - \tfrac{1}{2}\theta_{12})\hat{\mathbf{z}}, \end{aligned}\tag{20}$$

$$\begin{aligned}\hat{\mathbf{r}}_2 &= [\cos\alpha\cos\beta\cos(\gamma + \tfrac{1}{2}\theta_{12}) - \sin\alpha\sin(\gamma + \tfrac{1}{2}\theta_{12})]\hat{\mathbf{x}}\\ &\quad+[\sin\alpha\cos\beta\cos(\gamma + \tfrac{1}{2}\theta_{12}) + \cos\alpha\sin(\gamma + \tfrac{1}{2}\theta_{12})]\hat{\mathbf{y}}\\ &\quad-\sin\beta\cos(\gamma + \tfrac{1}{2}\theta_{12})\hat{\mathbf{z}}. \end{aligned}\tag{21}$$

Note that $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$ are interchanged by changing the sign of θ_{12}.

Since θ_1 and ϕ_1, and θ_2 and ϕ_2, are the polar and azimuthal angles of $\mathbf{r}_1$ and $\mathbf{r}_2$ relative to the space-fixed frame, we have the following useful relations which summarize the transformation from $(\theta_1, \phi_1, \theta_2, \phi_2)$ to $(\alpha, \beta, \gamma, \theta_{12})$ [see Eqs. (20) and (21)]:

$$\cos\theta_1 = -\sin\beta\cos(\gamma - \tfrac{1}{2}\theta_{12}), \tag{22}$$

$$\cos\theta_2 = -\sin\beta\cos(\gamma + \tfrac{1}{2}\theta_{12}), \tag{23}$$

$$\begin{aligned}\sin(\theta_1)e^{\pm i\phi_1} &= e^{\pm i\alpha}[\cos\beta\cos(\gamma - \tfrac{1}{2}\theta_{12})\\ &\quad\pm i\sin(\gamma - \tfrac{1}{2}\theta_{12})], \end{aligned}\tag{24}$$

$$\begin{aligned}\sin(\theta_2)e^{\pm i\phi_2} &= e^{\pm i\alpha}[\cos\beta\cos(\gamma + \tfrac{1}{2}\theta_{12})\\ &\quad\pm i\sin(\gamma + \tfrac{1}{2}\theta_{12})]. \end{aligned}\tag{25}$$

III. ANGULAR-MOMENTUM OPERATORS

The one-particle angular-momentum operators in the space-fixed frame are, suppressing the subscript 1 or 2 temporarily,

$$l_z = -i\frac{\partial}{\partial\phi}, \tag{26}$$

$$\boldsymbol{l}^2 = -\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right), \tag{27}$$

$$l_\pm = e^{\pm i\phi}\left(\pm\frac{\partial}{\partial\theta} + i\cot\theta\frac{\partial}{\partial\phi}\right), \tag{28}$$

where $l_\pm = l_x \pm il_y$. Note that ζ^l is an eigenfunction of both $\boldsymbol{l}^2$ and l_z, with eigenvalues $l(l+1)$ and l, respectively.

The total angular momentum operator in the space-fixed frame is $\mathbf{L} = \boldsymbol{l}_1 + \boldsymbol{l}_2$, and the total angular-momentum raising and lowering operators are $L_\pm = l_{\pm,1} + l_{\pm,2}$. We want to express these operators in terms of derivatives with respect to the Euler angles, and to this end we first show that

$$L_z = -i\frac{\partial}{\partial\alpha}. \tag{29}$$

We can verify Eq. (29) by writing

$$\frac{\partial}{\partial\alpha} = A_1\frac{\partial}{\partial\phi_1} + A_2\frac{\partial}{\partial\phi_2} + B_1\frac{\partial}{\partial\theta_1} + B_2\frac{\partial}{\partial\theta_2}, \tag{30}$$

and letting $\partial/\partial\alpha$ act on both sides of Eqs. (22)–(25) to yield the coefficients A_1, A_2, B_1, and B_2. Thus, letting $\partial/\partial\alpha$ act on both sides of Eq. (22) gives $B_1 = 0$, and doing the same with Eqs. (23)–(25) gives $B_2 = 0$, $A_1 = A_2 = 1$, thereby establishing Eq. (29).

In a similar fashion we can verify that

$$L_\pm = e^{\pm i\alpha}\left[\pm\frac{\partial}{\partial\beta} + \frac{i}{\sin\beta}\left(\cos\beta\frac{\partial}{\partial\alpha} - \frac{\partial}{\partial\gamma}\right)\right]. \tag{31}$$

Since L_z and $L_\pm$ do not contain derivatives with respect to θ_{12}, we can use Eqs. (29) and (31) to express derivatives with respect to the Euler angles in terms of L_x, L_y, and L_z; we find, in addition to Eq. (29), that

$$-i\frac{\partial}{\partial\beta} = -\sin(\alpha)L_x + \cos(\alpha)L_y, \tag{32}$$

$$-i\frac{\partial}{\partial\gamma} = \cos(\alpha)\sin(\beta)L_x + \sin(\alpha)\sin(\beta)L_y + \cos(\beta)L_z. \tag{33}$$

Noting that $\mathbf{L}^2 = \frac{1}{2}(L_+L_- + L_-L_+) + L_z^2$ we also have from Eqs. (29) and (31)

$$\mathbf{L}^2 = -\left[\frac{\partial^2}{\partial\beta^2} + \cot\beta\frac{\partial}{\partial\beta} + \frac{1}{\sin^2\beta}\left(\frac{\partial^2}{\partial\alpha^2} + \frac{\partial^2}{\partial\gamma^2}\right) - 2\frac{\cot\beta}{\sin\beta}\frac{\partial^2}{\partial\alpha\partial\gamma}\right]. \tag{34}$$

The invariance of $\mathbf{L}^2$ under the interchange of α and γ suggests it would be useful to introduce new angular-momentum operators defined by interchanging α and γ:

$$L'_z = -i\frac{\partial}{\partial\gamma}, \tag{35}$$

$$L'_\pm = e^{\pm i\gamma}\left[\pm\frac{\partial}{\partial\beta} + \frac{i}{\sin\beta}\left(\cos\beta\frac{\partial}{\partial\gamma} - \frac{\partial}{\partial\alpha}\right)\right]. \tag{36}$$

We have, of course, $\mathbf{L}'^2 = \mathbf{L}^2$, and combining Eqs. (35) and (36) with Eqs. (29), (32), and (33), using Eqs. (14)–(16), we can see that

$$L'_z = \hat{\mathbf{z}}' \cdot \mathbf{L}, \tag{37}$$

$$L'_\pm = (-\hat{\mathbf{x}}' \pm i\hat{\mathbf{y}}') \cdot \mathbf{L}. \tag{38}$$

Hence $\mathbf{L}'$ is an angular momentum operator in the body-fixed frame (but note that its projection along the x' axis is $-L'_x$ rather than L'_x). As is well known, $\mathbf{L}^2$ ($=\mathbf{L}'^2$), L_z, and L'_z are a commuting set of operators whose eigenfunctions are the rotation matrices $\mathcal{D}_L^{M,K}(\alpha,\beta,\gamma)$, with K the eigenvalue of L'_z (see, e.g., Ref. [1]).

IV. FACTORIZATION OF ONE-PARTICLE ANGULAR-MOMENTUM OPERATOR

In the space-fixed frame the one-particle angular-momentum operator $\boldsymbol{l}_1^2$ has the simple and well-known factorization

$$\boldsymbol{l}_1^2 = -\frac{1}{\sin^2\theta_1}\left(\sin\theta_1\frac{\partial}{\partial\theta_1} + i\frac{\partial}{\partial\phi_1}\right)\left(\sin\theta_1\frac{\partial}{\partial\theta_1} - i\frac{\partial}{\partial\phi_1}\right). \tag{39}$$

More generally, if we introduce the three functions $f_\pm$ and χ, with

$$f_+f_- = 1, \tag{40}$$

we can factorize $\boldsymbol{l}_1^2$ as

$$\boldsymbol{l}_1^2 = -f_-\left(\frac{\partial}{\partial\theta_1} + \frac{i}{\sin\theta_1}\frac{\partial}{\partial\phi_1} + \chi\right) \times f_+\left(\frac{\partial}{\partial\theta_1} - \frac{i}{\sin\theta_1}\frac{\partial}{\partial\phi_1}\right), \tag{41}$$

where, taking into account Eq. (40),

$$\chi = \cot\theta_1 - \left(\frac{\partial f_+}{\partial\theta_1} + \frac{i}{\sin\theta_1}\frac{\partial f_+}{\partial\phi_1}\right)/f_+ \tag{42}$$

$$= \left[\left(\frac{\partial}{\partial\theta_1} + \frac{i}{\sin\theta_1}\frac{\partial}{\partial\phi_1}\right)(f_-\sin\theta_1)\right]/(f_-\sin\theta_1). \tag{43}$$

We recover Eq. (39) by putting $f_+ = \sin\theta_1$ (which yields $\chi = 0$). We now express the operators

$$\frac{\partial}{\partial\theta_1} \pm \frac{i}{\sin\theta_1}\frac{\partial}{\partial\phi_1}$$

in terms of derivatives with respect to θ_{12} and the Euler angles, thereby obtaining a factorization of $\boldsymbol{l}_1^2$ which is useful in simplifying the two-electron-atom Hamiltonian.

Referring to Eq. (21) we see that $\mathbf{r}_2$ depends on γ and θ_{12} through the combination $\gamma + \frac{1}{2}\theta_{12}$. It follows that, with C and D angle-dependent coefficients,

$$\frac{\partial}{\partial\theta_{12}} - \frac{1}{2}\frac{\partial}{\partial\gamma} = \frac{C}{\sin\theta_1}\frac{\partial}{\partial\phi_1} + D\frac{\partial}{\partial\theta_1}. \tag{44}$$

Letting both sides of Eq. (44) act on $\cos\theta_1$, using Eq. (22), yields

$$\sin\beta\sin(\gamma - \tfrac{1}{2}\theta_{12}) = D\sin\theta_1. \tag{45}$$

Letting both sides of Eq. (44) act on $\sin\theta_1 e^{\pm i\phi_1}$, using Eq. (24), yields

$$e^{\pm i\alpha}[\cos\beta\sin(\gamma - \tfrac{1}{2}\theta_{12}) \mp i\cos(\gamma - \tfrac{1}{2}\theta_{12})] = [\pm iC + D\cos\theta_1]e^{\pm i\phi_1}. \tag{46}$$

Solving Eqs. (45) and (46) for C and D gives

$$C = -\cos\beta/\sin\theta_1, \tag{47}$$

$$D = \sin\beta\sin(\gamma - \tfrac{1}{2}\theta_{12})/\sin\theta_1. \tag{48}$$

Note that $C^2 + D^2 = 1$.

Equation (44) is one of two identities that we need to accomplish our goal. The second identity is based on the observation that, since $\mathbf{r}\cdot\boldsymbol{l}\equiv 0$, the operator $\hat{\mathbf{r}}_2\cdot\mathbf{L}$ is simply $\hat{\mathbf{r}}_2\cdot\boldsymbol{l}_1$, and therefore involves only derivatives with respect to the angles of $\mathbf{r}_1$. Hence, with C' and D' angle-dependent coefficients, we can write

$$\hat{\mathbf{r}}_2\cdot\mathbf{L} = -i\sin(\theta_{12})\left(\frac{C'}{\sin\theta_1}\frac{\partial}{\partial\phi_1}+D'\frac{\partial}{\partial\theta_1}\right). \tag{49}$$

Now, putting $\alpha=\beta=\gamma=0$ on the right-hand side of Eq. (21) (so the unprimed and primed coordinate systems coincide) gives

$$\hat{\mathbf{r}}_2 = \cos(\tfrac{1}{2}\theta_{12})\hat{\mathbf{x}}' + \sin(\tfrac{1}{2}\theta_{12})\hat{\mathbf{y}}', \tag{50}$$

so that [recall Eq. (38)]

$$\begin{aligned}\hat{\mathbf{r}}_2\cdot\mathbf{L} &= -\cos(\tfrac{1}{2}\theta_{12})L'_x + \sin(\tfrac{1}{2}\theta_{12})L'_y\\ &= -\tfrac{1}{2}(e^{i\theta_{12}/2}L'_+ + e^{-i\theta_{12}/2}L'_-).\end{aligned} \tag{51}$$

Letting both sides of Eq. (49) act on $\cos\theta_1$, using Eqs. (51), (36), and (22), yields

$$\cos(\beta)/\sin\theta_1 = D'. \tag{52}$$

Letting both sides of Eq. (49) act on $\sin\theta_1 e^{\pm i\phi_1}$, using Eqs. (51), (36), and (24), yields

$$-e^{\pm i\alpha}\sin\beta = [\pm iC' + D'\cos\theta_1]e^{\pm i\phi_1}. \tag{53}$$

Solving Eqs. (52) and (53) for C' and D' gives

$$C' = D, \tag{54}$$

$$D' = -C. \tag{55}$$

It follows from Eqs. (44), (49), (54), and (55) that

$$\frac{\partial}{\partial\theta_{12}} - \frac{1}{2}\frac{\partial}{\partial\gamma} \pm \frac{\hat{\mathbf{r}}_2\cdot\mathbf{L}}{\sin\theta_{12}} = (D\pm iC)\left(\frac{\partial}{\partial\theta_1}\mp\frac{i}{\sin\theta_1}\frac{\partial}{\partial\phi_1}\right). \tag{56}$$

This suggests that we choose $f_\pm = D\pm iC$, which is consistent with Eq. (40) since $C^2+D^2=1$. Hence, from Eqs. (41) and (56), we have, using Eq. (51),

$$\begin{aligned}\boldsymbol{l}_1^2 = &-\left(\frac{\partial}{\partial\theta_{12}} - \frac{1}{2}\frac{\partial}{\partial\gamma} + \frac{e^{i\theta_{12}/2}L'_+ + e^{-i\theta_{12}/2}L'_-}{2\sin\theta_{12}} + \chi f_-\right)\\ &\times\left(\frac{\partial}{\partial\theta_{12}} - \frac{1}{2}\frac{\partial}{\partial\gamma} - \frac{e^{i\theta_{12}/2}L'_+ + e^{-i\theta_{12}/2}L'_-}{2\sin\theta_{12}}\right).\end{aligned} \tag{57}$$

It remains to determine χ. Since

$$f_\pm = [\sin\beta\sin(\gamma-\tfrac{1}{2}\theta_{12}) \mp i\cos\beta]/\sin\theta_1, \tag{58}$$

we have, using the left-hand side of Eq. (56) to carry out the differentiation on the right-hand side of Eq. (43),

$$\chi = \cot(\theta_{12})/f_-. \tag{59}$$

Consequently, if we introduce

$$P_1 \equiv X_1 + Y_1 + \cot\theta_{12}, \tag{60}$$

$$Q_1 \equiv X_1 - Y_1, \tag{61}$$

where X_1 and Y_1 are the operators

$$X_1 \equiv \frac{\partial}{\partial\theta_{12}} - \frac{1}{2}\frac{\partial}{\partial\gamma}, \tag{62}$$

$$Y_1 \equiv \frac{e^{i\theta_{12}/2}L'_+ + e^{-i\theta_{12}/2}L'_-}{2\sin\theta_{12}}, \tag{63}$$

$\boldsymbol{l}_1^2$ has the factorization

$$\boldsymbol{l}_1^2 = -P_1Q_1. \tag{64}$$

Similarly, $\boldsymbol{l}_2^2$ has the factorization

$$\boldsymbol{l}_2^2 = -P_2Q_2, \tag{65}$$

where

$$P_2 \equiv X_2 + Y_2 + \cot\theta_{12}, \tag{66}$$

$$Q_2 \equiv X_2 - Y_2, \tag{67}$$

and where X_2 and Y_2 are the operators

$$X_2 \equiv \frac{\partial}{\partial\theta_{12}} + \frac{1}{2}\frac{\partial}{\partial\gamma}, \tag{68}$$

$$Y_2 \equiv \frac{e^{-i\theta_{12}/2}L'_+ + e^{i\theta_{12}/2}L'_-}{2\sin\theta_{12}}. \tag{69}$$

V. LAPLACIAN

The Laplacian for both electrons is

$$\nabla_1^2+\nabla_2^2 = \frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} - \frac{\boldsymbol{l}_1^2}{r_1^2} - \frac{\boldsymbol{l}_2^2}{r_2^2}. \tag{70}$$

Since we have expressed, through Eqs. (60)–(69), the one-particle angular-momentum operators in terms of $L'_z(=-i\partial/\partial\gamma)$, $L'_\pm$, and $\partial/\partial\theta_{12}$, we could easily work out the effect of applying the Laplacian to a finite linear combination of the rotation matrices. Recall that the rotation matrices are eigenfunctions of L_z, L'_z, and $\mathbf{L}'^2$ $(=\mathbf{L}^2)$, and that both $L_\pm$ and $L'_\pm$ are raising and lowering operators (see the Appendix). Thereby we could reduce the energy-eigenvalue problem to a set of coupled radial equations. (Ultimately we change variables from θ_{12} to r_3.) These equations would be similar to those derived by Bhatia and Temkin [4]. However, as noted in the Introduction, we obtain a simpler set of radial equations if we apply the Laplacian to the terms on the right-hand side of Eq. (5) or (6). We first do this for the case $\Pi=(-1)^L$, i.e., we apply the Laplacian to the terms $\zeta_1^{l_1}\zeta_2^{l_2}g$ where $g\equiv r_1^{l_1}r_2^{l_2}f^L_{l_1,l_2}(r_1,r_2,r_3)$. We make use of the factorization of $\boldsymbol{l}_1^2$ and $\boldsymbol{l}_2^2$ developed in the preceding section, noting the following properties. (i) The action of X_1 on a function of $\mathbf{r}_2$ only, or the action of X_2 on a function of $\mathbf{r}_1$ only, yields zero; recall that $\mathbf{r}_1$ depends on γ and θ_{12} through the combination $\gamma-\frac{1}{2}\theta_{12}$, while $\mathbf{r}_2$ depends on γ and θ_{12} through the combination $\gamma+\frac{1}{2}\theta_{12}$ — see Eqs. (20) and (21). (ii) The action of Y_1 on a function of $\mathbf{r}_2$ only, or the action of Y_2 on a function of $\mathbf{r}_1$ only, yields zero; recall that $Y_1=-(\hat{\mathbf{r}}_2\cdot\boldsymbol{l}_1)/\sin(\theta_{12})$

and $Y_2 = -(\hat{\mathbf{r}}_1 \cdot \boldsymbol{l}_2)/\sin(\theta_{12})$. (iii) The action of Y_1 or Y_2 on a function of r_1, r_2, and r_3 only (e.g., the function g) yields zero since such a function is invariant under a rotation (it is independent of the Euler angles) so that the action of $L'_{\pm}$ yields zero.

Using these properties, along with Eqs. (60)–(64), and observing that $X_1 g = \partial g/\partial\theta_{12}$, noting that later we change variables from θ_{12} to r_3, we obtain

$$\begin{aligned}
-\boldsymbol{l}_1^2\zeta_1^{l_1}\zeta_2^{l_2}g &= (P_1Q_1)\zeta_1^{l_1}\zeta_2^{l_2}g \\
&= P_1\left[(Q_1\zeta_1^{l_1})\zeta_2^{l_2}g + \zeta_1^{l_1}\zeta_2^{l_2}\frac{\partial g}{\partial\theta_{12}}\right] \\
&= \zeta_2^{l_2}\left[(Q_1\zeta_1^{l_1})(P_1-\cot\theta_{12})g + (P_1Q_1\zeta_1^{l_1})g + +(P_1\zeta_1^{l_1})\frac{\partial g}{\partial\theta_{12}} + \zeta_1^{l_1}(P_1-\cot\theta_{12})\frac{\partial g}{\partial\theta_{12}}\right] \\
&= \zeta_2^{l_2}\left[\frac{\partial g}{\partial\theta_{12}}(P_1+Q_1)\zeta_1^{l_1} - g\boldsymbol{l}_1^2\zeta_1^{l_1} + \zeta_1^{l_1}\frac{\partial^2 g}{\partial\theta_{12}^2}\right].
\end{aligned} \tag{71}$$

Since $P_1+Q_1 = 2X_1+\cot\theta_{12}$, and since $\boldsymbol{l}_1^2\zeta_1^{l_1} = l_1(l_1+1)\zeta_1^{l_1}$, we have

$$\begin{aligned}
-\boldsymbol{l}_1^2\zeta_1^{l_1}\zeta_2^{l_2}g = \zeta_2^{l_2}\bigg[&\frac{\partial g}{\partial\theta_{12}}(2X_1+\cot\theta_{12})\zeta_1^{l_1} \\
&-l_1(l_1+1)\zeta_1^{l_1}g + \zeta_1^{l_1}\frac{\partial^2 g}{\partial\theta_{12}^2}\bigg].
\end{aligned} \tag{72}$$

Next, we show that

$$X_1\zeta_1^{l_1} = l_1\cot(\theta_{12})\zeta_1^{l_1} - \frac{l_1}{\sin\theta_{12}}\zeta_1^{l_1-1}\zeta_2. \tag{73}$$

We start by noting that from Eqs. (22) and (62) we have

$$X_1\cos\theta_1 = -\sin\beta\sin(\gamma-\theta_{12}/2). \tag{74}$$

We can rewrite the right-hand side of Eq. (74) using

$$\begin{aligned}
&-\sin\theta_{12}\sin(\gamma-\theta_{12}/2) \\
&\quad = \cos(\gamma+\theta_{12}/2) - \cos(\gamma-\theta_{12}/2)\cos\theta_{12}.
\end{aligned} \tag{75}$$

From Eqs. (22), (23), (74), and (75) we obtain

$$X_1\cos\theta_1 = \cot\theta_{12}\cos\theta_1 - \frac{\cos\theta_2}{\sin\theta_{12}}. \tag{76}$$

Applying L_+ to both sides of Eq. (76) gives

$$X_1\zeta_1 = \cot(\theta_{12})\zeta_1 - \frac{\zeta_2}{\sin\theta_{12}}, \tag{77}$$

and using $X_1\zeta_1^n = n\zeta_1^{n-1}X_1\zeta_1$ yields Eq. (73). This yields finally

$$\begin{aligned}
-\boldsymbol{l}_1^2\zeta_1^{l_1}\zeta_2^{l_2}g = \zeta_1^{l_1}\zeta_2^{l_2}\bigg[&\frac{\partial^2}{\partial\theta_{12}^2} + \cot(\theta_{12})\frac{\partial}{\partial\theta_{12}} \\
&+l_1\left(2\cot(\theta_{12})\frac{\partial}{\partial\theta_{12}} - (l_1+1)\right)\bigg]g \\
&-\zeta_1^{l_1-1}\zeta_2^{l_2+1}\frac{2l_1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}g.
\end{aligned} \tag{78}$$

A similar equation holds for $\boldsymbol{l}_2^2$; we replace $\boldsymbol{l}_1^2$ by $\boldsymbol{l}_2^2$, and interchange l_1 and l_2, and ζ_1 and ζ_2.

Collecting together the results obtained so far in this section, we have

$$\begin{aligned}
(\nabla_1^2+\nabla_2^2)\zeta_1^{l_1}\zeta_2^{l_2}g = \zeta_1^{l_1}\zeta_2^{l_2}&\left[\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\left(\frac{\partial^2}{\partial\theta_{12}^2} + \cot(\theta_{12})\frac{\partial}{\partial\theta_{12}}\right)\right]g \\
+\zeta_1^{l_1}\zeta_2^{l_2}&\left[\frac{l_1}{r_1^2}\left(2\cot(\theta_{12})\frac{\partial}{\partial\theta_{12}} - (l_1+1)\right) + \frac{l_2}{r_2^2}\left(2\cot(\theta_{12})\frac{\partial}{\partial\theta_{12}} - (l_2+1)\right)\right]g \\
-\zeta_1^{l_1-1}\zeta_2^{l_2+1}&\frac{2l_1}{r_1^2\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}g - \zeta_1^{l_1+1}\zeta_2^{l_2-1}\frac{2l_2}{r_2^2\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}g.
\end{aligned} \tag{79}$$

We can change variables from θ_{12} to r_3 by using $r_3^2 = r_1^2+r_2^2-2r_1r_2\cos\theta_{12}$. After some straightforward algebra we obtain, upon including the Coulomb potentials, the desired result given by Eqs. (8)–(10) for the case of parity $\Pi = (-1)^L$.

We now outline how the result given by Eqs. (11) and (12), for the case of parity $\Pi = -(-1)^L$, can be obtained. We start by noting a few identities involving the operators X_1 and Y_1 of Eqs. (62) and (63) and $\Theta \equiv e^{i\alpha}\sin\beta$: (i) $X_1\Theta = 0$; (ii)$Y_1\Theta = -i[\cot(\theta_{12})\zeta_2 - \zeta_1/\sin\theta_{12}]/\sin\theta_{12}$; (iii) $X_1Y_1\Theta = -\cot(\theta_{12})Y_1\Theta$; (iv) $Y_1\zeta_1 = -i\Theta$; (v) $Y_1^2\Theta = \Theta/(\sin^2\theta_{12})$. We briefly outline their proof. The relation (i) follows since $\Theta = e^{i\alpha}\sin\beta$ does not depend on either γ or θ_{12}. The action of Y_1 is easily calculated by applying the expression for $L'_\pm$; see Eq. (31). Hence it is straightforward to obtain (iv). Similarly, we obtain $Y_1\Theta = \xi_2/\sin\theta_{12}$ where $\xi_2 = e^{i\alpha}[\cos(\gamma+\theta_{12}/2) + i\sin(\gamma+\theta_{12}/2)\cos\beta]$. After some simple manipulation ξ_2 can be expressed as $\xi_2 = -i[\cot(\theta_{12})\zeta_2 - \zeta_1/\sin\theta_{12}]$, thus proving (ii). Since $X_1\xi_2 = 0$ we have $X_1Y_1\Theta = \xi_2X_1(1/\sin\theta_{12}) = -\xi_2\cot(\theta_{12})/\sin\theta_{12}$, and now relation (iii) follows immediately. Using (ii), and (iv) in the second step, we get $Y_1^2\Theta = iY_1\zeta_1/(\sin^2\theta_{12}) = \Theta/(\sin^2\theta_{12})$, thus proving (v). Proceeding in a similar way as we did in deriving Eq. (78) we obtain

$$-\boldsymbol{l}_1^2\Theta\zeta_1^{l_1}\zeta_2^{l_2}g = -\Theta\boldsymbol{l}_1^2\zeta_1^{l_1}\zeta_2^{l_2}g + \Theta\zeta_1^{l_1-1}\zeta_2^{l_2+1}\frac{2l_1\cot\theta_{12}}{\sin\theta_{12}}g - \frac{(2l_1+1)}{\sin^2\theta_{12}}\Theta\zeta_1^{l_1}\zeta_2^{l_2}g. \quad (80)$$

Replacing g by $g\sin\theta_{12}$ in Eq. (80) and Eq. (78) and combining Eqs. (78) and (80) gives

$$-\boldsymbol{l}_1^2\Theta\sin(\theta_{12})\zeta_1^{l_1}\zeta_2^{l_2}g = \Theta\sin(\theta_{12})\zeta_1^{l_1}\zeta_2^{l_2}\left[\frac{\partial^2}{\partial\theta_{12}^2} + \cot(\theta_{12})\frac{\partial}{\partial\theta_{12}} + (l_1+1)\left(2\cot(\theta_{12})\frac{\partial}{\partial\theta_{12}} - (l_1+2)\right)\right]g$$
$$-\Theta\sin(\theta_{12})\zeta_1^{l_1-1}\zeta_2^{l_2+1}\frac{2l_1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}g. \quad (81)$$

A similar expression holds for $-\boldsymbol{l}_2^2\Theta\sin(\theta_{12})\zeta_1^{l_1}\zeta_2^{l_2}g$. This yields

$$(\nabla_1^2+\nabla_2^2)\Theta\sin(\theta_{12})\zeta_1^{l_1}\zeta_2^{l_2}g$$
$$= \Theta\sin(\theta_{12})\zeta_1^{l_1}\zeta_2^{l_2}\left[\frac{\partial^2}{\partial r_1^2} + \frac{2}{r_1}\frac{\partial}{\partial r_1} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2}\frac{\partial}{\partial r_2} + \left(\frac{1}{r_1^2}+\frac{1}{r_2^2}\right)\left(\frac{\partial^2}{\partial\theta_{12}^2} + \cot(\theta_{12})\frac{\partial}{\partial\theta_{12}}\right)\right]g$$
$$+\Theta\sin(\theta_{12})\zeta_1^{l_1}\zeta_2^{l_2}\left[\frac{(l_1+1)}{r_1^2}\left(2\cot(\theta_{12})\frac{\partial}{\partial\theta_{12}} - (l_1+2)\right) + \frac{(l_2+1)}{r_2^2}\left(2\cot(\theta_{12})\frac{\partial}{\partial\theta_{12}} - (l_2+2)\right)\right]g$$
$$-\Theta\sin(\theta_{12})\zeta_1^{l_1-1}\zeta_2^{l_2+1}\frac{2l_1}{r_1^2\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}g - \Theta(\sin\theta_{12})\zeta_1^{l_1+1}\zeta_2^{l_2-1}\frac{2l_2}{r_2^2\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}g. \quad (82)$$

Changing variables from θ_{12} to r_{12}, we obtain after some straightforward algebra Eqs. (11) and (12).

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APPENDIX

In this Appendix we make contact with the work of Bhatia and Temkin [4]. The Euler angles (Φ,Θ,Ψ) used by Bhatia and Temkin differ only very slightly from our Euler angles (α,β,γ); we have $\alpha = \Phi - \pi/2$, $\beta = \Theta$, and $\gamma = \Psi$.

1. Laplacian

We first show that our factorized expression for $\boldsymbol{l}_1^2$, given by Eqs. (60)–(64), i.e.,

$$\boldsymbol{l}_1^2 = -(X_1 + Y_1 + \cot\theta_{12})(X_1 - Y_1), \quad (A1)$$

is equivalent to the expression of Eqs. (63) and (64) of Bhatia and Temkin:

$$-\boldsymbol{l}_1^2 = \frac{\partial^2}{\partial\theta_{12}^2} + \cot(\theta_{12})\frac{\partial}{\partial\theta_{12}} + \frac{1}{2\sin^2\theta_{12}}\{-\mathbf{L}^2 + \cos(\theta_{12})[\sin(2\gamma)\,\Lambda_2 - \cos(2\gamma)\,\Lambda_1]$$
$$+\sin(\theta_{12})[\sin(2\gamma)\,\Lambda_1 + \cos(2\gamma)\,\Lambda_2]\} - \frac{\partial^2}{\partial\theta_{12}\partial\gamma} - \tfrac{1}{2}\cot(\theta_{12})\frac{\partial}{\partial\gamma} + \left(\frac{1}{4} - \frac{1}{2\sin^2\theta_{12}}\right)\frac{\partial^2}{\partial^2\gamma}, \quad (A2)$$

$$\Lambda_1 \equiv 2\frac{\partial^2}{\partial\beta^2} + \frac{\partial^2}{\partial\gamma^2} + \mathbf{L}^2, \quad (A3)$$

$$\Lambda_2 \equiv 2\frac{\cot\beta}{\sin\beta}\frac{\partial}{\partial\alpha} - (1+2\cot^2\beta)\frac{\partial}{\partial\gamma} - \frac{2}{\sin\beta}\frac{\partial^2}{\partial\beta\partial\alpha} + 2\cot(\beta)\frac{\partial^2}{\partial\beta\partial\gamma}. \quad (A4)$$

It follows from the equivalence of the expressions for l_1^2 that the expressions for the Laplacian are also equivalent. Noting that

$$[X_1, Y_1] = -\cot(\theta_{12}) Y_1, \tag{A5}$$

we have, from Eq. (A1),

$$-l_1^2 = X_1^2 - Y_1^2 + \cot(\theta_{12}) X_1. \tag{A6}$$

Substituting our explicit expressions for X_1 and Y_1 [see Eqs. (60)–(64)], and using

$$L'_+ L'_- + L'_- L'_+ = 2(\mathbf{L}'^2 - L_z'^2), \\ = 2\left(\mathbf{L}^2 + \frac{\partial^2}{\partial \gamma^2}\right), \tag{A7}$$

yields

$$-l_1^2 = \frac{\partial^2}{\partial \theta_{12}^2} + \cot(\theta_{12}) \frac{\partial}{\partial \theta_{12}} - \frac{1}{\sin^2 \theta_{12}} \left[e^{i\theta_{12}} \left(\frac{L_+'^2}{2}\right) + e^{-i\theta_{12}} \left(\frac{L_-'^2}{2}\right) + \tfrac{1}{2}\mathbf{L}^2 \right] \tag{A8}$$

$$-\frac{\partial^2}{\partial \theta_{12} \partial \gamma} - \tfrac{1}{2}\cot(\theta_{12}) \frac{\partial}{\partial \gamma} + \left(\frac{1}{4} - \frac{1}{2\sin^2 \theta_{12}}\right) \frac{\partial^2}{\partial^2 \gamma}. \tag{A9}$$

This expression is equivalent to Eqs. (A2)–(A4) if we can identify

$$L_\pm'^2 = e^{\pm 2i\gamma} (\Lambda_1 \pm i\Lambda_2). \tag{A10}$$

These identities may be readily established upon squaring $L'_\pm$, utilizing Eq. (36), and comparing with Eqs. (A3) and (A4).

2. Transformation between different expansions

Now we derive the connection between the coefficients $f_K^L(r_1, r_2, r_3)$ in the expansion of Eq. (2), which is similar to Bhatia and Temkin's expansion, and the coefficients $f_{l_1,l_2}^L(r_1, r_2, r_3)$ of Eqs. (5) and (6), which lead to the generalized Breit equations, Eq. (13). With a conveniently chosen phase for the rotation matrices $\mathcal{D}_L^{M,K}(\alpha, \beta, \gamma)$, the result is

$$f_K^L(r_1, r_2, r_3) = \sum_{l_1+l_2=L} r_1^{l_1} r_2^{l_2} f_{l_1,l_2}^L(r_1, r_2, r_3) C_{l_1,l_2}^K(\theta_{12}) \tag{A11}$$

for the case of $\Pi = (-1)^L$, while

$$f_K^L(r_1, r_2, r_3) \\ = 2 r_1 r_2 \sin(\theta_{12}) \\ \times \sum_{l_1+l_2=L-1} r_1^{l_1} r_2^{l_2} f_{l_1,l_2}^L(r_1, r_2, r_3) C_{l_1,l_2}^K(\theta_{12}) \tag{A12}$$

for the case of $\Pi = -(-1)^L$. In the above equations the functions $C_{l_1,l_2}^K(\theta_{12})$ are given by [with ${}_2F_1$ a hypergeometric function]

$$C_{l_1,l_2}^K(\theta_{12}) = \frac{(-1)^{(l_1+l_2-K)/2}}{N_L^K} \frac{l_1!}{[(l_1-l_2-K)/2]![(l_1+l_2+K)/2]!} \\ \times e^{-i(l_2+K/2)\theta_{12}}\ {}_2F_1(-\tfrac{1}{2}(l_1+l_2+K), -l_2, \tfrac{1}{2}(l_1-l_2-K)+1, e^{2i\theta_{12}}), \tag{A13}$$

with

$$N_L^K = (-1)^L \left[\frac{(2L+1)}{8\pi^2} \frac{(2L)!}{(L-K)!(L+K)!} \right], \tag{A14}$$

valid for both parity cases. Note the symmetry property $C_{l_1,l_2}^K(\theta_{12}) = C_{l_2,l_1}^K(-\theta_{12})$.

Let us start by defining the rotation matrices $\mathcal{D}_L^{M,K}(\alpha, \beta, \gamma)$, with our phase convention:

$$\mathcal{D}_L^{M,K}(\alpha, \beta, \gamma) = (-1)^{[|K-M|+K+M]/2} N_L^{M,K} \sin^{|K-M|}(\beta/2) \cos^{|K+M|}(\beta/2) e^{iM\alpha} e^{iK\gamma} \\ \times {}_2F_1[-L + \tfrac{1}{2}|K-M| + \tfrac{1}{2}|K+M|, L + \tfrac{1}{2}|K-M| + \tfrac{1}{2}|K+M| \\ +1, 1 + |K-M|, \sin^2(\beta/2)], \tag{A15}$$

where the normalization constant $N_L^{M,K}$ is

$$N_L^{M,K} = \left[\frac{(2L+1)}{8\pi^2} \frac{(L + \frac{1}{2}|K+M| + \frac{1}{2}|K-M|)!}{(L - \frac{1}{2}|K+M| - \frac{1}{2}|K-M|)!} \frac{(L - \frac{1}{2}|K+M| + \frac{1}{2}|K-M|)!}{(L + \frac{1}{2}|K+M| - \frac{1}{2}|K-M|)!} \right]^{1/2} \frac{1}{|K-M|!}. \tag{A16}$$

Note that $\mathcal{D}_L^{M,K}(\alpha,\beta,\gamma) = \mathcal{D}_L^{K,M}(\beta,\alpha,\gamma)$. Our phase convention is in accord with

$$L_\pm \mathcal{D}_l^{M,K} = \sqrt{(L\mp M)(L\pm M+1)}\mathcal{D}_l^{M\pm1,K} \quad \text{(A17)}$$

and

$$L'_\pm \mathcal{D}_l^{M,K} = \sqrt{(L\mp K)(L\pm K+1)}\mathcal{D}_l^{M,K\pm1}. \quad \text{(A18)}$$

It suffices to consider the case $M = L$, for which the rotation matrices take a particularly simple form:

$$\mathcal{D}_M^{L,K}(\alpha,\beta,\gamma) = N_L^K e^{iL\alpha} e^{iK\gamma} \sin^{L-K}(\beta/2)\cos^{L+K}(\beta/2). \quad \text{(A19)}$$

To prove Eqs. (A11) and (A12) we first invoke Eqs. (24) and (25):

$$\zeta_1 = e^{i\alpha}[\cos^2(\beta/2)e^{i(\gamma-\theta_{12}/2)} - \sin^2(\beta/2)e^{-i(\gamma-\theta_{12}/2)}] \quad \text{(A20)}$$

$$\zeta_2 = e^{i\alpha}[\cos^2(\beta/2)e^{i(\gamma+\theta_{12}/2)} - \sin^2(\beta/2)e^{-i(\gamma+\theta_{12}/2)}]. \quad \text{(A21)}$$

Some simple algebraic manipulations readily yield

$$\zeta_1^{l_1}\zeta_2^{l_2} = \sum_{K=-L,(-1)^K=(-1)^L}^{L} \mathcal{D}_L^{L,K}(\alpha,\beta,\gamma)C_{l_1,l_2}^K(\theta_{12}) \quad \text{(A22)}$$

for the case of $\Pi = (-1)^L$, while

$$\tfrac{1}{2}\sin(\beta)e^{i\alpha}\zeta_1^{l1}\zeta_2^{l2} = \sum_{K=-L,(-1)^K=-(-1)^L}^{L} \mathcal{D}_L^{L,K}(\alpha,\beta,\gamma)C_{l_1,l_2}^K(\theta_{12}), \quad \text{(A23)}$$

for the case of $\Pi = -(-1)^L$. Substitution of these expansions into Eqs. (5) and (6), respectively, and comparing with Eq. (2), yields Eqs. (A11) and (A12).

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