Special Topics on Precision Measurement in Atomic Physics: Lecture 4

Hylleraas Coordinates

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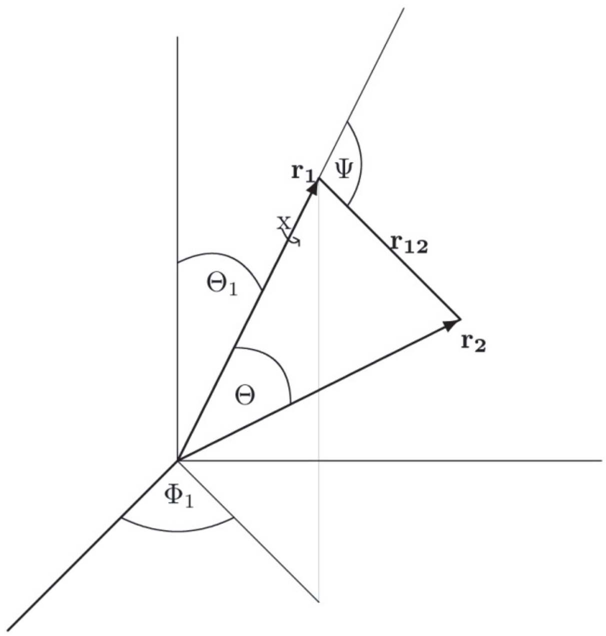
Matrix Elements of $\boldsymbol{H}$

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{Z^{-1}}{r_{12}} \tag{1}$$

Taking r_1, r_2 and r_{12} as independent variables,

$$\begin{aligned}\nabla_1^2 \;&=\; \frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r_{12}^2}\frac{\partial}{\partial r_{12}}\left(r_{12}^2\frac{\partial}{\partial r_{12}}\right)\\ &\quad - \frac{l_1(l_1+1)}{r_1^2} + 2(r_1 - r_2\cos\theta_{12})\frac{1}{r_{12}}\frac{\partial^2}{\partial r_1\partial r_{12}}\\ &\quad - 2(\nabla_1^Y\cdot\mathbf{r}_2)\frac{1}{r_{12}}\frac{\partial}{\partial r_{12}}\end{aligned}$$

where ∇_1^Y acts only on the spherical harmonic part of the wave function and the diagram



defines the complete set of 6 independent variables is r_1, r_2, r_{12}, θ_1, φ_1, χ. If r_{12} were not an independent variable, then one could take the volume element to be

$$d\tau = r_1^2\, dr_1 \sin\theta_1\, d\theta_1\, d\varphi_1 r_2^2\, dr_2 \sin\theta_2\, d\theta_2\, d\varphi_2. \tag{2}$$

However, θ_2 and φ_2 are no longer independent variables. To eliminate them, take the point $\mathbf{r}_1$ as the origin of a new polar co-ordinate system, and write

$$d\tau = -r_1^2\, dr_1 \sin\theta_1\, d\theta_1\, d\varphi_1\, r_{12}^2\, dr_{12} \sin\psi\, d\psi\, d\chi \tag{3}$$

and use

$$r_2^2 = r_1^2 + r_{12}^2 + 2r_1 r_{12} \cos\psi \tag{4}$$

Then for fixed r_1 and r_{12},

$$2r_2 dr_2 = -2r_1 r_{12} \sin\psi\, d\psi \tag{5}$$

Thus

$$d\tau = r_1 dr_1\, r_2 dr_2\, r_{12} dr_{12}\, \sin\theta_1\, d\theta_1\, d\varphi_1\, d\chi \tag{6}$$

The basic type of integral to be calculated is

$$\begin{aligned} I\left(l_1, m_1, l_2, m_2; R\right) &= \int \sin\left(\theta_1\right) d\theta_1 d\varphi_1 d\chi Y_{l_1}^{m_1 *}\left(\theta_1, \varphi_1\right) Y_{l_2}^{m_2}\left(\theta_2, \varphi_2\right) \\ &\quad \times \int r_1 dr_1\, r_2 dr_2\, r_{12} dr_{12}\, R\left(r_1, r_2, r_{12}\right) \end{aligned}$$

Consider first the angular integral. $Y_{l_2}^{m_2}(\theta_2, \varphi_2)$ can be expressed in terms of the independent variables $\theta_1, \varphi_1, \chi$ by use of the rotation matrix relation

$$Y_{l_2}^{m_2}(\theta_2, \varphi_2) = \sum_m \mathcal{D}^{(l_2)}_{m_2,m}(\varphi_1, \theta_1, \chi)^* Y_{l_2}^{m}(\theta_{12}, \varphi) \tag{7}$$

where θ_{12}, φ are the polar angles of $\mathbf{r}_2$ relative to $\mathbf{r}_1$. The angular integral is then

$$\begin{aligned} I_{\text{ang}} &= \int_0^{2\pi} d\chi \int_0^{2\pi} d\varphi_1 \int_0^{\pi} \sin(\theta_1)\, d\theta_1 Y_{l_1}^{m_1}(\theta_1, \varphi_1)^* \\ &\quad \times \sum_m \mathcal{D}^{(l_2)}_{m_2,m}(\varphi_1, \theta_1, \chi)^* \, Y_{l_2}^{m}(\theta_{12}, \varphi) \end{aligned}$$

Use

$$Y_{l_1}^{m_1}(\theta_1, \varphi_1)^* = \sqrt{\frac{2l_1+1}{4\pi}} \mathcal{D}^{(l_1)}_{m_1,0}(\varphi_1, \theta_1, \chi) \tag{8}$$

together with the orthogonality property of the rotation matrices (Brink and Satchler, p 147)

$$\begin{aligned} &\int \mathcal{D}^{(j)*}_{m,m'} \mathcal{D}^{(J)}_{M,M'} \sin\theta_1 \, d\theta_1 \, d\varphi_1 \, d\chi \\ &= \frac{8\pi^2}{2j+1} \delta_{jJ} \, \delta_{mM} \, \delta_{m'M'} \end{aligned}$$

to obtain

$$\begin{aligned} I_{\text{ang}} &= \sqrt{\frac{2l_1+1}{4\pi}} \frac{8\pi^2}{2l_1+1} \delta_{l_1,l_2} \delta_{m_1,m_2} Y_{l_2}^{0}(\theta_{12}, \varphi) \\ &= 2\pi \delta_{l_1,l_2} \delta_{m_1,m_2} P_{l_2}(\cos\theta_{12}) \end{aligned}$$

since

$$Y_{l_2}^{0}(\theta_{12}, \varphi) = \sqrt{\frac{2l_1+1}{4\pi}} P_{l_2}(\cos\theta_{12}) \tag{9}$$

Note that $P_{l_2}(\cos\theta_{12})$ is just a short hand expression for a radial function because

$$\cos\theta_{12} = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2} \tag{10}$$

The original integral is thus

$$\begin{aligned} I(l_1, m_1, l_2, m_2; R) &= 2\pi \delta_{l_1,l_2} \delta_{m_1,m_2} \int_0^{\infty} r_1 \, dr_1 \int_0^{\infty} r_2 \, dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12} \, dr_{12} \\ &\quad \times R(r_1, r_2, r_{12}) \, P_{l_2}(\cos\theta_{12}) \end{aligned}$$

where again

$$\cos\theta_{12} = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2} \tag{11}$$

is a purely radial function.

The above would become quite complicated for large l_2 because $P_{l_2}(\cos\theta_{12})$ contains terms up to $(\cos\theta_{12})^{l_2}$. However, recursion relations exist which allow any integral containing $P_l\,(\cos\theta_{12})$ in terms of those containing just $P_0\,(\cos\theta_{12}) = 1$ and $P_1\,(\cos\theta_{12}) = \cos\theta_{12}$.

RADIAL INTEGRALS AND RECURSION RELATIONS

The basic radial integral is [see G.W.F. Drake, Phys. Rev. A **18**, 820 (1978)]

$$\begin{aligned} I_0\,(a,b,c) &= \int_0^\infty r_1 dr_1 \int_{r_1}^\infty r_2\, dr_2 \int_{r_2-r_1}^{r_1+r_2} r_{12}\, dr_{12}\, r_1^a\, r_2^b\, r_{12}^c\, e^{-\alpha r_1 - \beta r_2} \\ &\quad + \int_0^\infty r_2 dr_2 \int_{r_2}^\infty r_1\, dr_1 \int_{r_1-r_2}^{r_1+r_2} r_{12}\, dr_{12}\, r_1^a r_2^b r_{12}^c\, e^{-\alpha r_1 - \beta r_2} \\ &= \frac{2}{c+2} \sum_{i=0}^{[(c+1)/2]} \binom{c+2}{2i+1} \left\{ \frac{q!}{\beta^{q+1}\,(\alpha+\beta)^{p+1}} \sum_{j=0}^{q} \frac{(p+j)!}{j!} \left(\frac{\beta}{\alpha+\beta}\right)^j \right. \\ &\quad \left. + \frac{q'!}{\alpha^{q'+1}\,(\alpha+\beta)^{p'+1}} \sum_{j=0}^{q'} \frac{(p'+j)!}{j!} \left(\frac{\alpha}{\alpha+\beta}\right)^j \right\} \end{aligned}$$

where

$$\begin{aligned} p &= a + 2i + 2 \qquad & p' &= b + 2i + 2 \\ q &= b + c - 2i + 2 \qquad & q' &= a + c - 2i + 2 \end{aligned}$$

The above applies for $a, b \geq -2, c \geq -1$. $[x]$ means "greatest integer in" x.

Then

$$\begin{aligned} I_1\,(a,b,c) &= \int d\tau_r\, r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} P_1\,(\cos\theta) \\ &= \frac{1}{2}\left[I_0\,(a+1, b-1, c) + I_0\,(a-1, b+1, c) - I_0\,(a-1, b-1, c+2)\right] \end{aligned}$$

The Radial Recursion Relation

Recall that the full integral is

$$I(l_1 m_1, l_2 m_2; R) = 2\pi \delta_{l_1,l_2}\, \delta_{m_1,m_2}\, I_{l_2}(R) \tag{12}$$

where, for any function $R = R(r_1, r_2, r_{12})$

$$I_{l_2}(R) = \int d\tau_r \, R(r_1, r_2, r_{12}) P_{l_2}(\cos\theta_{12}) \tag{13}$$

and $\int d\tau_r$ stands for the radial part of the integral

$$\int d\tau_r \, (\cdots) = \int_0^\infty r_1 \, dr_1 \int_0^\infty r_2 \, dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r_{12} \, dr_{12} \, (\cdots)$$

To obtain the recursion relation, use

$$P_l(x) = \frac{[P'_{l+1}(x) - P'_{l-1}(x)]}{2l+1} \tag{14}$$

with

$$P'_{l+1}(x) = \frac{d}{dx} P_{l+1}(x) \tag{15}$$

Here $x = \cos\theta_{12}$ and

$$\begin{aligned} \frac{d}{d\cos\theta_{12}} &= \frac{dr_{12}}{d\cos\theta_{12}} \frac{d}{dr_{12}} \\ &= -\frac{r_1 r_2}{r_{12}} \frac{d}{dr_{12}} \end{aligned}$$

Then,

$$I_l(R) = -\int d\tau_r \, R \, \frac{r_1 r_2}{r_{12}} \frac{d}{dr_{12}} \frac{[P_{l+1}(\cos\theta_{12}) - P_{l-1}(\cos\theta_{12})]}{2l+1} \tag{16}$$

The r_{12} part of the integral can be integrated by parts to obtain

$$\begin{aligned} &\int_{|r_1-r_2|}^{r_1+r_2} r_{12} \, dr_{12} \, R \, \frac{r_1 r_2}{r_{12}} \frac{d}{dr_{12}} [P_{l+1} - P_{l-1}] \\ &= R r_1 r_2 [P_{l+1} - P_{l-1}] \Big|_{|r_1-r_2|}^{r_1+r_2} - \int_{|r_1-r_2|}^{r_1+r_2} r_{12} \, dr_{12} \left(\frac{d}{dr_{12}} R \right) \frac{r_1 r_2}{r_{12}} \frac{[P_{l+1} - P_{l-1}]}{2l+1} \end{aligned}$$

The integrated term vanishes because

$$\cos\theta_{12} = \frac{r_1^2 + r_2^2 - r_{12}^2}{2 r_1 r_2} \quad \begin{aligned} &= -1 \quad \text{when} \quad r_{12}^2 = (r_1 + r_2)^2 \\ &= 1 \quad\;\;\, \text{when} \quad r_{12}^2 = (r_1 - r_2)^2 \end{aligned} \tag{17}$$

and $P_l(1) = 1$, $P_l(-1) = (-1)^l$. Thus,

$$I_{l+1}\left(\frac{r_1 r_2}{r_{12}} R' \right) = (2l+1) \, I_l(R) - I_{l-1}\left(\frac{r_1 r_2}{r_{12}} R' \right) \tag{18}$$

If

$$R = r_1^{a-1} r_2^{b-1} r_{12}^{c+2} e^{-\alpha r_1 - \beta r_2} \tag{19}$$

then [G.W.F. Drake, Phys. Rev. A **18**, 820 (1978)]

$$I_{l+1}(r_1^a r_2^b r_{12}^c) = \frac{2l+1}{c+2} I_l \left(r_1^{a-1} r_2^{b-1} r_{12}^{c+2} \right) + I_{l-1} \left(r_1^a r_2^b r_{12}^c \right) \tag{20}$$

For the special case $c = -2$, take

$$R = r_1^{a-1} r_2^{b-1} \ln r_{12} e^{-\alpha r_1 - \beta r_2} \tag{21}$$

Then

$$I_{l+1} \left(r_1^a r_2^b r_{12}^{-2} \right) = I_l \left(r_1^{a-1} r_2^{b-1} \ln r_{12} \right) (2l+1) - I_{l-1} \left(r_1^a r_2^b r_{12}^{-2} \right) \tag{22}$$

This allows all I_l integrals to be calculated from tables of I_0 and I_1 integrals.

THE GENERAL INTEGRAL

The above results for the angular and radial integrals can now be combined into a general formula for integrals of the type

$$I = \int\int d\mathbf{r}_1 \, d\mathbf{r}_2 \, R_1 \mathcal{Y}^{M'}_{l_1' l_2' L'} (\hat{r}_1, \hat{r}_2) \, T^{Q}_{k_1 k_2 K} (\mathbf{r}_1, \mathbf{r}_2) \, R_2 \mathcal{Y}^{M}_{l_1 l_2 L} (\hat{r}_1, \hat{r}_2) \tag{23}$$

where

$$\mathcal{Y}^{M}_{l_1 l_2 L} (\hat{r}_1, \hat{r}_2) = \sum_{m_1, m_2} \langle l_1 l_2 m_1 m_2 | LM \rangle Y_{l_1}^{m_1} (\hat{r}_1) \, Y_{l_2}^{m_2} (\hat{r}_2) \tag{24}$$

and

$$T^{Q}_{k_1 k_2 K} (\mathbf{r}_1, \mathbf{r}_2) = \sum_{q_1, q_2} \langle k_1 k_2 q_1 q_2 | KQ \rangle Y_{k_1}^{q_1} (\hat{r}_1) \, Y_{k_2}^{q_2} (\hat{r}_2) \tag{25}$$

The basic idea is to make repeated use of the formula

$$\begin{aligned} Y_{l_1}^{m_1} (\hat{r}_1) \, Y_{l_2}^{m_2} (\hat{r}_1) \; &= \; \sum_{lm} \left(\frac{(2l_1+1)(2l_2+1)(2l+1)}{4\pi} \right)^{1/2} \\ &\times \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} Y_l^{m*} (\hat{r}_1) \end{aligned} \tag{26}$$

where

$$Y^{m*}(\hat{r}) = (-1)^m Y_l^{-m}(\hat{r}) \tag{27}$$

and

$$\begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} = \frac{(-1)^{l_1-l_2-m}}{(2l+1)^{1/2}} \langle l_1 l_2 m_1 m_2 | l, -m \rangle \tag{28}$$

is a 3-j symbol. In particular, write

$$Y_{l_1'}^{m_1'}(\hat{r}_1)^* \underbrace{Y_{k_1}^{q_1}(\hat{r}_1)\, Y_{l_1}^{m_1}(\hat{r}_1)}_{\sum_{\lambda_1\mu_1} Y_{\lambda_1}^{\mu_1}(\hat{r}_1)} \quad = \quad \sum_{\Lambda M}(\ldots) Y_\Lambda^M(\hat{r}_1)$$

$$Y_{l_2'}^{m_2'}(\hat{r}_2) \underbrace{Y_{k_2}^{q_2}(\hat{r}_2)\, Y_{l_2}^{m_2}(\hat{r}_2)}_{\sum_{\lambda_2\mu_2} Y_{\lambda_2}^{\mu_2}(\hat{r}_2)} \quad = \quad \sum_{\Lambda' M'}(\ldots)\, Y_{\Lambda'}^{M'*}(\hat{r}_2)$$

The angular integral then gives a factor of $2\pi\delta_{\Lambda,\Lambda'}\delta_{M,M'}P_\Lambda(\cos\theta_{12})$. The total integral therefore reduces to the form

$$I = \sum_\Lambda C_\Lambda I_\Lambda(R_1 R_2) \tag{29}$$

where $C_\Lambda = \sum_{\lambda_1,\lambda_2} C_{\lambda_1,\lambda_2,\Lambda}$. For further details and derivations, including graphical representations, see G.W.F. Drake, Phys. Rev. A **18**, 820 (1978).

Matrix Elements of H

Recall that

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{Z^{-1}}{r_{12}} \tag{30}$$

Consider matrix elements of

$$\begin{aligned} \nabla_1^2 \;=\; & \frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{(\vec{l}_1^Y)^2}{r_1^2} + \frac{2\left(r_1 - r_2\cos\theta\right)}{r}\frac{\partial^2}{\partial r_1 \partial r} \\ & - 2\left(\nabla_1^Y \cdot \mathbf{r}_2\right)\frac{1}{r}\frac{\partial}{\partial r} \end{aligned} \tag{31}$$

where $r \equiv r_{12}$ and $\cos\theta \equiv \cos\theta_{12}$. Also in what follows, define $\hat{\nabla}_1^Y \equiv r_1\nabla_1^Y$ where ∇^Y operates only on the spherical harmonic part of the wave function, and similarly for $\vec{l}_1^Y$.

A general matrix element is

$$\langle r_1^{a'} r_2^{b'} r_{12}^{c'} e^{-\alpha' r_1 - \beta' r_2} \mathcal{Y}_{l_1' l_2' L'}^{M'}(\hat{r}_1, \hat{r}_2) \left|\nabla_1^2\right| r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1 l_2 L}^{M}(\hat{r}_1, \hat{r}_2)\rangle \tag{32}$$

Since ∇_1^2 is rotationally invariant, this vanishes unless $L = L'$, $M = M'$. Also ∇_1^2 is Hermitian, so that the result must be the same whether it operates to the right or left, even though the results look very different. In fact, requiring the results to be the same yields some interesting and useful integral identities as follows:

Put

$$\mathcal{F} = F\mathcal{Y}_{l_1 l_2 L}^{M}\left(\hat{r}_1, \hat{r_2}\right) \tag{33}$$

and

$$F = r_1^a r_2^b r_{12}^c e^{-\alpha r_1 - \beta r_2} \tag{34}$$

Then

$$\begin{aligned} \nabla_1^2 \mathcal{F} \ = \ & \left\{ \frac{1}{r_1^2}\left[a\left(a+1\right) - l_1\left(l_1+1\right)\right] + \frac{c\left(c+1\right)}{r^2} + \alpha^2 - \frac{2\alpha\left(a+1\right)}{r_1} \right. \\ & \left. + \frac{2\left(r_1 - r_2\cos\theta\right)}{r_1 r^2} c\left[a - \alpha r_1\right] - \frac{2c}{r^2}\left(\hat{\nabla}_1^Y \cdot \hat{r}_2\right)\frac{r_2}{r_1} \right\} \mathcal{F} \end{aligned} \tag{35}$$

and

$$\begin{aligned} \left\langle \mathcal{F}' \left| \nabla_1^2 \right| \mathcal{F} \right\rangle \ = \ & \sum_\Lambda \int d\tau_r \ F' C_\Lambda\left(1\right) P_\Lambda\left(\cos\theta\right) \\ & \times \left\{ \frac{1}{r_1^2}\left[a\left(a+1\right) - l_1\left(l_1+1\right)\right] - \frac{2\alpha\left(a+1\right)}{r_1} + \frac{c\left(c+1\right)}{r^2} \right. \\ & \left. + \alpha^2 + \frac{2\left(r_2 - r_2\cos\theta\right)}{r_1 r^2} c\left(a - \alpha r_1\right) \right\} F \qquad (36) \\ & + \sum_\Lambda \int d\tau_{,r} \ F' C_\Lambda\left(\hat{\nabla}_1^Y \cdot \hat{r}_2\right) P_\Lambda\left(\cos\theta\right)\left(\frac{-2cr_2}{r_1 r^2}\right) F \qquad (37) \end{aligned}$$

where

$$\int d\tau_r = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r\, dr \tag{38}$$

For brevity, let the sum over Λ and the radial integrations be understood, and let $\left(\nabla_1^2\right)$ stand for the terms that appear in the integrand. Then operating to the right gives

$$\begin{aligned} (\nabla_1^2)_R \ = \ & \frac{1}{r_1^2}\left[a\left(a+1\right) - l_1\left(l_1+1\right)\right] + \frac{c\left(c+1\right)}{r^2} + \alpha^2 - \frac{2\alpha\left(a+1\right)}{r_1} \\ & + \frac{2\left(r_1 - r_2\cos\theta\right)}{r_1 r^2} c\left(a - \alpha r_1\right) - \frac{2cr_2}{r_1 r^2}\left(\hat{\nabla}_1^Y \cdot \hat{r}_2\right) \end{aligned} \tag{39}$$

Operating to the left gives

$$
\begin{aligned}
(\nabla_1^2)_L &= \frac{1}{r_1^2}\left[a'\left(a'+1\right)-l_1'\left(l_1'+1\right)\right]+\frac{c'\left(c'+1\right)}{r^2}+\alpha'^2-\frac{2\alpha'\left(a'+1\right)}{r_1} \\
&\quad+\frac{2\left(r_1-r_2\cos\theta\right)}{r_1r^2}c'\left(a'-\alpha' r_1\right)-\frac{2c'r_2}{r_1r^2}\left(\hat{\nabla}_1^{Y'}\cdot\hat{r}_2\right)
\end{aligned}
\tag{40}
$$

Now put

$$
\begin{aligned}
a_+ = a+a', &\quad \hat{\nabla}_1^+ = \hat{\nabla}_1^Y+\hat{\nabla}_1^{Y'} \\
a_- = a-a', &\quad \hat{\nabla}_1^- = \hat{\nabla}_1^Y-\hat{\nabla}_1^{Y'}
\end{aligned}
$$

etc., and substitute $a' = a_+ - a$, $c' = c_+ - c$, and $\alpha' = \alpha_+ - \alpha$ in $(\nabla_1^2)_L$. If a_+, c_+ and α_+ are held fixed, then the equation

$$
(\nabla_1^2)_R = (\nabla_1^2)_L \tag{41}
$$

must be true for arbitrary a, c, and α. Their coefficients must thus vanish.

This yields the integral relations

$$
\frac{\left(r_1-r_2\cos\theta\right)}{r_1r^2}=\frac{1}{c_+}\left(\frac{-\left(a_++1\right)}{r_1^2}+\frac{\alpha_+}{r_1}\right) \tag{42}
$$

from the coefficient of a, and

$$
\frac{\left(r_1-r_2\cos\theta\right)\left(a_+-\alpha_+r_1\right)}{r_1r^2}=\frac{r_2}{r_1r^2}\left(\hat{r}_2\cdot\hat{\nabla}_1^+\right)-\frac{\left(c_++1\right)}{r^2} \tag{43}
$$

from the coefficient of c. The coefficient of α gives an equation equivalent to (42).

Furthermore, if can be show that (see problem)

$$
\begin{aligned}
&\sum_\Lambda\int d\tau_r\,\frac{r^c}{r^2}C_\Lambda\left(\hat{r}_2\cdot\hat{\nabla}_1^Y\right)P_\Lambda\left(\cos\theta\right) \\
=\;&\sum_\Lambda\int d\tau_r\,\frac{r^c}{cr_1r_2}C_\Lambda\left(1\right)P_\Lambda\left(\cos\theta\right)\left(\frac{l_1'\left(l_1'+1\right)-l_1\left(l_1+1\right)-\Lambda\left(\Lambda+1\right)}{2}\right)
\end{aligned}
$$

and similarly for $\left(\hat{r}_2\cdot\hat{\nabla}_1^{Y'}\right)$ with l_1 and l_1' interchanged, then it follows that

$$
\frac{r^{c_+}}{r^2}\left(\hat{r}_2\cdot\hat{\nabla}_1^+\right)=-\frac{r^{c_+}}{c_+r_1r_2}\Lambda\left(\Lambda+1\right) \tag{44}
$$

and

$$\frac{r^{c_+}}{r^2}\left(\hat{r}_2 \cdot \hat{\nabla}_1^-\right) = \frac{r^{c_+}}{c_+ r_1 r_2}\left[l_1'\left(l_1'+1\right) - l_1\left(l_1+1\right)\right] \tag{45}$$

where equality applies after integration and summation over Λ.

Thus Eq. (43) becomes

$$\frac{\left(r_1 - r_2\cos\theta\right)\left(a_+ - \alpha_+ r_1\right)}{r_1 r^2} = -\frac{\Lambda\left(\Lambda+1\right)}{c_+ r_1^2} - \frac{\left(c_+ + 1\right)}{r^2} \tag{46}$$

Problem

Prove the integral relation

$$\begin{aligned}
& \sum_\Lambda \int d\tau_r\, f\left(r_1, r_2\right) \frac{1}{r}\left(\frac{d}{dr} g(r)\right) C_\Lambda\left(\hat{r}_2 \cdot \hat{\nabla}_1^Y\right) P_\Lambda\left(\cos\theta\right) \\
= \quad & \sum_\Lambda \int d\tau_r \frac{f\left(r_1, r_2\right)}{r_1, r_2} g(r) C_\Lambda\left(1\right) P_\Lambda\left(\cos\theta\right) \\
& \times\left(\frac{l_1'\left(l_1'+1\right) - l_1\left(l_1+1\right) - \Lambda\left(\Lambda+1\right)}{2}\right)
\end{aligned} \tag{47}$$

where $g(r)$ is an arbitrary function of r and the coefficients $C_\Lambda\left(1\right)$ are the angular coefficients from the overlap integral

$$\int d\Omega\, \mathcal{Y}_{l_1' l_2' L}^{M*}(\hat{r}_1, \hat{r}_2)\, \mathcal{Y}_{l_1 l_2 L}^{M}(\hat{r}_1, \hat{r}_2) = \sum_\Lambda C_\Lambda(1) P_\Lambda(\cos\theta_{12}).$$

Hint: Use the fact that l_1^2 is Hermitian so that

$$\int d\tau\, (l_1^2 \mathcal{Y}')^* g(r) \mathcal{Y} = \int d\tau\, \mathcal{Y}'^* l_1^2 (g(r)\mathcal{Y})$$

with $\vec{l}_1 = \frac{1}{i}\vec{r}_1 \times \nabla_1$. It is also useful to use

$$\cos\theta\, P_L(\cos\theta) \;=\; \frac{1}{2L+1}\left[L\, P_{L-1}(\cos\theta) + (L+1) P_{L+1}(\cos\theta)\right] \tag{48}$$

$$\begin{aligned}
& (\cos^2\theta - 1) P_L(\cos\theta) \\
= \; & \frac{L(L-1)}{(2L-1)(2L+1)} P_{L-2}(\cos\theta) - \frac{2(L^2+L-1)}{(2L-1)(2L+3)} P_L(\cos\theta)
\end{aligned}$$

$$
\begin{aligned}
&+ \frac{(L+1)(L+2)}{(2L+1)(2L+3)}P_{L+2}(\cos\theta) \\
&= \frac{L(L-1)}{(2L-1)(2L+1)}[P_{L-2}(\cos\theta) - P_L(\cos\theta)] \\
&+ \frac{(L+1)(L+2)}{(2L+1)(2L+3)}[P_{L+2}(\cos\theta) - P_L(\cos\theta)] \qquad (49)
\end{aligned}
$$

together with a double application of the integral recursion relation

$$
I_{L+1}\left(\frac{1}{r}\frac{d}{dr}g(r)\right) = (2L+1)I_L\left(\frac{1}{r_1r_2}g(r)\right) + I_{L-1}\left(\frac{1}{r}\frac{d}{dr}g(r)\right)
$$

Of course

$$
l_1^2\mathcal{Y}^M_{l_1l_2L}(\hat{r}_1,\hat{r}_2) = l_1(l_1+1)\mathcal{Y}^M_{l_1l_2L}(\hat{r}_1,\hat{r}_2)
$$

Begin by expanding

$$
l_1^2(g\mathcal{Y}) = \mathcal{Y}l_1^2 g + g\, l_1^2\mathcal{Y} + 2(\vec{l}_1 g)\cdot(\vec{l}_1\mathcal{Y})
$$

and show that

$$
\begin{aligned}
(\vec{l}_1 g)\cdot(\vec{l}_1\mathcal{Y}) &= \frac{r_1^2}{r}\frac{dg}{dr}\vec{r}_2\cdot\nabla_1\mathcal{Y} \quad \text{and} \qquad (50)\\
l_1^2 g(r) &= 2r_1r_2\cos\theta\frac{1}{r}\frac{dg}{dr} + r_1^2r_2^2(\cos^2\theta-1)\frac{1}{r}\frac{d}{dr}\left(\frac{1}{r}\frac{dg}{dr}\right). \qquad (51)
\end{aligned}
$$

The proof amounts to showing that the term $l_1^2 g(r)$ can be replaced by $\Lambda(\Lambda+1)g(r)$ after multiplying by $P_\Lambda(\cos\theta)$ and integrating by parts with respect to the radial integrations over r_1, r_2 and $r \equiv |\vec{r}_1 - \vec{r}_2|$. Remember that $\cos\theta$ is just a short-hand notation for the radial function $(r_1^2 + r_2^2 - r^2)/(2r_1r_2)$.

General Hermitian Property

The requirement that the various operators appearing in the Hamiltonian be Hermitian implies some very interesting and useful properties that lead to a symmetric form of the Hamiltonian matrix elements that are simple to evaluate for states of arbitrary angular momentum. Again for brevity, let $\langle f\rangle_R$ stand for the matrix element $\langle\mathcal{F}'\,|\mathcal{O}|\,\mathcal{F}\rangle$ of some Hermitian operator $\mathcal{O}$ acting to the right, and $\langle f\rangle_L$ the same operator acting to the left (such as ∇_1^2 or $\nabla_1\cdot\nabla_2$). Then each combination of terms of the form

$$
\langle f\rangle_R = a^2 f_1 + af_2 + abf_3 + b^2 f_4 + bf_5 + af_6\nabla_1^Y + bf_7\nabla_2^Y + f_8(Y) \qquad (52)
$$

acting to the right can be rewritten

$$\begin{aligned}\langle f\rangle_L &= (a_+-a)^2 f_1 + (a_+-a)f_2 + (a_+-a)(b_+-b)f_3 + (b_+-b)^2 f_4 \\ &\quad + (b_+-b)f_5 + (a_+-a)f_6\nabla_1^{Y\prime} + (b_+-b)f_7\nabla_2^{Y\prime} + f_8(Y')\end{aligned}$$

acting to the left, where as usual ∇_1^Y acts only on the spherical harmonic part of the wave function denoted for short by Y, and and integration over the rhs is assumed. Since these must be equal for arbitrary a and b,

$$a_+^2 f_1 + a_+f_2 + a_+b_+f_3 + b_+f_4 + b_+f_5 + a_+f_6\nabla_1^{Y\prime} + b_+f_7\nabla_2^{Y\prime} + f_8(Y') - f_8(Y) = 0 \tag{53}$$

Adding the corresponding expression with Y and Y' interchanged yields

$$a_+^2 f_1 + a_+f_2 + a_+b_+f_3 + b_+^2 f_4 + b_+f_5 + \frac{1}{2}a_+f_6\nabla_1^+ + \frac{1}{2}b_+f_7\nabla_2^+ = 0 \tag{54}$$

Subtracting gives

$$f_8(Y) - f_8(Y') = -\frac{1}{2}[a_+f_6\nabla_1^- + b_+f_7\nabla_2^-] \tag{55}$$

$$a[-2a_+f_1 - 2f_2 - b_+f_3 - f_6\nabla_1^+] = 0 \tag{56}$$

$$b[-2b_+f_4 - 2f_5 - a_+f_3 - f_7\nabla_2^+] = 0 \tag{57}$$

Adding the two forms gives

$$\begin{aligned}\langle f\rangle_R + \langle f\rangle_L = \frac{1}{2}(a_+^2 + a_-^2)f_1 + a_+f_2 + \frac{1}{2}(a_+b_+ + a_-b_-)f_3 \\ +\frac{1}{2}(b_+^2 + b_-^2)f_4 + b_+f_5 + \frac{1}{2}f_6(a_+\nabla_1^+ + a_-\nabla_1^-) \\ +\frac{1}{2}(b_+\nabla_2^+ + b_-\nabla_2^-) + f_8(Y) + f_8(Y')\end{aligned}$$

Subtracting $\frac{x}{2}\times$ Eq. (54), where x is an arbitrary parameter, gives

$$\begin{aligned}\langle f\rangle_R + \langle f\rangle_L &= \frac{1}{2}[(1-x)a_+^2 + a_-^2]f_1 + (1-\frac{x}{2})a_+f_2 + \frac{1}{2}[(1-x)a_+b_+ + a_-b_-]f_3 \\ &\quad + \frac{1}{2}[(1-x)b_+^2 + b_-^2]f_4 + (1-\frac{x}{2})f_5b_+ + \frac{1}{2}f_6[(1-\frac{x}{2})a_+\nabla_1^+ + a_-\nabla_1^-] \\ &\quad + \frac{1}{2}f_7[(1-\frac{x}{2})b_+\nabla_2^+ + b_-\nabla_2^-] + f_8(Y) + f_8(Y')\end{aligned}$$

If we choose $x = 1$, then

$$\begin{aligned}\langle f\rangle_R + \langle f\rangle_L &= \frac{1}{2}[a_-^2 f_1 + a_+ f_2 + a_- b_- f_3 + b_-^2 f_4 + b_+ f_5 \\ &+ \left(\frac{1}{2}a_+\nabla_1^+ + a_-\nabla_1^-\right) f_6 + \left(\frac{1}{2}b_+\nabla_2^+ + b_-\nabla_2^-\right) f_7] + f_8(Y) + f_8(Y')\end{aligned}$$

The General Hermitian Property for arbitrary x then gives

$$\begin{aligned}\nabla_1^2 &= \frac{1}{4}\{\frac{1}{r_1^2}[(1-x)a_+^2 + a_-^2 + 2(1-\frac{x}{2})a_+ - 2[l_1(l_1+1) + l_1'(l_1'+1)] \\ &- \frac{2}{r_1}[(1-x)\alpha_+ a_+ + \alpha_- a_- + 2(1-\frac{x}{2})\alpha_+] + (1-x)\alpha_+^2 + \alpha_-^2] \\ &+ \frac{2(r_1 - r_2\cos\theta)}{r_1 r^2}[(1-x)(a_+ - \alpha_+ r_1)c_+ + (a_- - \alpha_- r_2)c_-] \\ &- \frac{2r_2}{r_1 r^2}[(1-\frac{x}{2})c_+\hat{r}_2\cdot\hat{\nabla}_1^+ + c_-\hat{r}_2\hat{\nabla}_1^-] + \frac{(1-x)c_+^2 + c_-^2 + 2(1-\frac{x}{2})c_+}{r^2}\}\end{aligned}$$

. Use [from Eqs. (44), (45), and (46)]

$$\begin{aligned}\frac{-2r_2}{r_1 r^2}[(1-\frac{x}{2})c_+\hat{r}_2\hat{\nabla}_1^+ + c_-\hat{r}_2\hat{\nabla}_1^-] &= \frac{2}{r_1^2}\Big[(1-\frac{x}{2})\Lambda(\Lambda+1) \\ &- \frac{c_-}{c_+}[l_1'(l_1'+1) + l_1(l_1+1)]\Big] \quad (58)\end{aligned}$$

$$\begin{aligned}\frac{2(r_1 - r_2\cos\theta)}{r_1 r^2}(a_- - \alpha_- r_1)c_- &= 2\frac{c_-}{c_+}\Big[\frac{-1}{r_1^2}[a_-(a_+ + 1)] \\ &+ \frac{1}{r_1}[a_-\alpha_+ + \alpha_-(a_+ + 2)] - \alpha_-\alpha_+\Big] \quad (59)\end{aligned}$$

$$(60)$$

and

$$\begin{aligned}\frac{2(r_1 - r_2\cos\theta)}{r_1 r^2}(a_+ - \alpha_+ r_1)c_+ &= 2\Big[-\frac{1}{r_1^2}[a_+(a_+ + 1)] \\ &+ \frac{1}{r_1}[a_+\alpha_+ + \alpha_+(a_+ + 2)] - \alpha_+^2\Big] \quad (61)\end{aligned}$$

.

Substituting into ∇_1^2 gives

$$
\begin{aligned}
\nabla_1^2 &= \frac{1}{4}\{\frac{1}{r_1^2}[-(1-x)a_+^2 + a_-^2 + xa_+ + 2(1-\frac{x}{2})\Lambda(\Lambda+1) \\
&\quad - 2l_1(l_1+1)(1-\frac{c_-}{c_+}) - 2l_1'(l_1'+1)(1+\frac{c_-}{c_+}) - \frac{2c_-a_-}{c_+}(a_++1)] \\
&\quad - \frac{2}{r_1}\left[-(1-x)\alpha_+(a_++2) + \alpha_-a_- + 2(1-\frac{x}{2})\alpha_+ - \frac{c_-}{c_+}[a_-\alpha_+ + \alpha_-(a_++2)]\right] \\
&\quad - (1-x)\alpha_+^2 + \alpha_-^2 - 2\frac{c_-}{c_+}\alpha_-\alpha_+ + \frac{1}{r^2}\left[(1-x)c_+^2 + c_-^2 + 2(1-\frac{x}{2})c_+\right]\}
\end{aligned}
$$

This has the form

$$
\nabla_1^2 = \frac{1}{4}\left[\frac{A_1}{r_1^2} + \frac{B_1}{r_1} + \frac{C_1}{r^2} + D_1\right] \tag{62}
$$

with

$$
\begin{aligned}
A_1(\Lambda) &= -(1-x)a_+^2 + a_-^2 + xa_+ + 2(1-\frac{x}{2})\Lambda(\Lambda+1) - 2l_1(l_1+1)(1-\frac{c_-}{c_+}) \\
&\quad - 2l_1'(l_1'+1)(1+\frac{c_-}{c_+}) - \frac{2c_-a_-}{c_+}(a_++1) && (63) \\
B_1 &= 2\left[(1-x)\alpha_+(a_++2) - \alpha_-a_- - 2(1-\frac{x}{2})\alpha_+\right. \\
&\quad \left. + \frac{c_-}{c_+}[a_-\alpha_+ + \alpha_-(a_++2)]\right] && (64) \\
C_1 &= (1-x)c_+^2 + c_-^2 + 2(1-\frac{x}{2})c_+ && (65) \\
D_1 &= -(1-x)\alpha_+^2 + \alpha_-^2 - 2\frac{c_-}{c_+}\alpha_-\alpha_+ && (66)
\end{aligned}
$$

Choose $x = 1$ to eliminate the large a_+^2 terms. The complete Hamiltonian is then (in Z-scaled a.u.)

$$
\begin{aligned}
H &= -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{Z^{-1}}{r} \\
&= -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{Z-1}{Zr_2} + Z^{-1}\left(\frac{1}{r} - \frac{1}{r_2}\right)
\end{aligned} \tag{67}
$$

The effective radial part H_Λ is then

$$H_\Lambda = -\frac{1}{8}\left[\frac{A_1(\Lambda)}{r_1^2} + \frac{B_1+8}{r_1} + \frac{C_1}{r^2} + D_1 + D_2 + \frac{A_2(\Lambda)}{r_2^2} + \frac{B_2+8(Z-1)/Z}{r_2} + \frac{C_2}{r^2}\right] + Z^{-1}\left(\frac{1}{r} - \frac{1}{r_2}\right) \qquad (68)$$

Interpretation

Eq. (68) defines the effective radial part H_Λ of the Hamiltonian operator H. H_Λ depends explicitly on Λ through the coefficients $A_1(\Lambda)$ and $A_2(\Lambda)$ (unless one chooses $x = 2$). Recall that, just as in Eq. (36), this just represents the integrand in an expression that must still be integrated over radial coordinates and summed over Λ to obtain the expression

$$\langle \mathcal{F}' | H | \mathcal{F} \rangle = \sum_\Lambda \int d\tau_r \, C_\Lambda(1) \, P_\Lambda(\cos\theta) \, F' H_\Lambda F \qquad (69)$$

where

$$\int d\tau_r = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r \, dr \qquad (70)$$

and the coefficients $C_\Lambda(1)$ are the coefficients corresponding to the simple overlap integral (i.e. $T_K^Q = T_0^0 = 1$) in the general angular integral (23).