

Special Topics on Precision Measurement in Atomic Physics: Lecture 4

Hylleraas Coordinates: Appendix

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ANGULAR COEFFICIENTS FOR MATRIX ELEMENTS OF H

Recall that the matrix elements of H have the form

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

where

$$\int d\tau_r = \int_0^{\infty} r_1 dr_1 \int_0^{\infty} r_2 dr_2 \int_{|r_1-r_2|}^{r_1+r_2} r dr \quad (2)$$

and

$$H_{\Lambda} = -\frac{1}{8} \left[\frac{A_1(\Lambda)}{r_1^2} + \frac{B_1 + 8}{r_1} + \frac{C_1}{r_2^2} + D_1 + D_2 + \frac{A_2(\Lambda)}{r_2^2} + \frac{B_2 + 8(Z-1)/Z}{r_2} + \frac{C_2}{r^2} \right] + Z^{-1} \left(\frac{1}{r} - \frac{1}{r_2} \right) \quad (3)$$

with $A_1(\Lambda)$, B_1 , C_1 , and D_1 defined by

$$A_1(\Lambda) = -(1-x)a_+^2 + a_-^2 + xa_+ + 2\left(1 - \frac{x}{2}\right)\Lambda(\Lambda+1) - 2l_1(l_1+1)\left(1 - \frac{c_-}{c_+}\right) - 2l_1'(l_1'+1)\left(1 + \frac{c_-}{c_+}\right) - \frac{2c_-a_-}{c_+}(a_++1) \quad (4)$$

$$B_1 = 2 \left[(1-x)\alpha_+(a_++2) - \alpha_-a_- - 2\left(1 - \frac{x}{2}\right)\alpha_+ + \frac{c_-}{c_+}[a_-\alpha_+ + \alpha_-(a_++2)] \right] \quad (5)$$

$$C_1 = (1-x)c_+^2 + c_-^2 + 2\left(1 - \frac{x}{2}\right)c_+ \quad (6)$$

$$D_1 = -(1-x)\alpha_+^2 + \alpha_-^2 - 2\frac{c_-}{c_+}\alpha_-\alpha_+ \quad (7)$$

and similarly for $A_2(\Lambda)$, B_2 , C_2 , and D_2 . One of the advantages of this formula is that it only requires the angular coefficients $C_{\Lambda}(1)$ corresponding

to the overlap integral. The general formula for these coefficients for states of arbitrary angular momentum L is [see G.W.F. Drake, Phys. Rev. A **18**, 820 (1978), Eq. (20)]

$$C_\Lambda(1) = \frac{(-1)^{L+\Lambda}}{2} (2\Lambda + 1) [(2l_1 + 1)(2l'_1 + 1)(2l_2 + 1)(2l'_2 + 1)]^{1/2} \\ \times \begin{pmatrix} l'_1 & l_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_2 & l_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & l_1 & l_2 \\ \Lambda & l'_2 & l'_1 \end{Bmatrix} \quad (8)$$

expressed in terms of 3- j and 6- j symbols. If one of the two electrons is in an s -state, then there is only one nonvanishing coefficient. For the direct integral with $l_1 = l'_1 = 0$ and $l_2 = l'_2 = L$, it is $C_0(1) = 1/2$ and for the corresponding exchange integral it is $C_L(1) = 1/2$.

ROLE OF DEPENDENT AND INDEPENDENT VARIABLES FOR THE GRADIENT OPERATOR ∇_1

There is a possible point of confusion concerning the effect of the gradient operator ∇_1 or ∇_1^2 acting on powers of r_{12} . Even though we are regarding r_{12} as an *independent* variable for the purposes of evaluating integrals, it remains (by definition) a *dependent* variable when calculating partial derivatives with respect to \mathbf{r}_1 while holding \mathbf{r}_2 fixed. By definition, the partial derivatives in ∇_1 mean “change \mathbf{r}_1 while holding \mathbf{r}_2 fixed,” and so $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ must necessarily change in concert. The correct procedure is easily seen by writing out the derivatives in cartesian coordinates with

$$\nabla_1 = \hat{\mathbf{i}} \frac{\partial}{\partial x_1} + \hat{\mathbf{j}} \frac{\partial}{\partial y_1} + \hat{\mathbf{k}} \frac{\partial}{\partial z_1} \quad (9)$$

and

$$r_{12} = [(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2]^{1/2} \quad (10)$$

It is then immediately obvious that

$$\nabla_1 r_{12} = \frac{1}{r_{12}} \left[\hat{\mathbf{i}}(x_1 - x_2) + \hat{\mathbf{j}}(y_1 - y_2) + \hat{\mathbf{k}}(z_1 - z_2) \right] \\ = \frac{\mathbf{r}_{12}}{r_{12}} \quad (11)$$

Similarly $\nabla_2 r_{12} = -\mathbf{r}_{12}/r_{12}$.

OPTIMIZATION OF NONLINEAR PARAMETERS

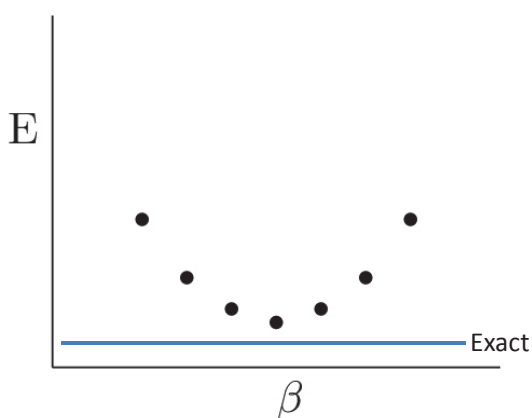
The traditional method of performing Hylleraas calculations is to write the basis set in the form

$$\Psi = \sum_{i,j,k} c_{i,j,k} \varphi_{i,j,k}(\alpha, \beta) \pm \text{exchange} \quad (12)$$

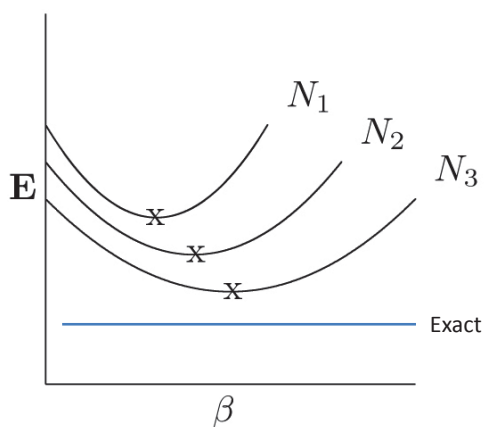
with

$$\varphi_{i,j,k}(\alpha, \beta) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1 l_2 L}^M. \quad (13)$$

The usual procedure is to set $\alpha = Z$ so that it represents the inner 1s electron, and then to vary β so as to minimize the energy.



Since β appears in Ψ as a nonlinear parameter, the entire calculation must be repeated for each value of β . However, the minimum becomes progressively lower as the basis set is enlarged.



Difficulties:

1. If the basis set is constructed so that $i + j + k \leq N$, the the number of terms is

$$(N + 1)(N + 2)(N + 3)/6 \quad (14)$$

For example, $N = 14$ already gives 680 terms and an accuracy of about 1 part in 10^{10} for low-lying states. A substantial improvement in accuracy would require much larger basis sets, together with multiple precision arithmetic to avoid loss of significant figures when high powers are included.

2. The accuracy rapidly deteriorates as one goes to more highly excited states—about 1 significant figure is lost each time the principle quantum number is increased.

Cure: Doubled Basis Sets

We have found that writing basis sets in the form

$$\begin{aligned} \Psi &= \sum_{i,j,k} \left[c_{i,j,k}^{(1)} \varphi_{ijk}(\alpha_1, \beta_1) + c_{ijk}^{(2)} \varphi_{ijk}(\alpha_2, \beta_2) \right] \pm \text{exchange} \\ &= \psi(\mathbf{r}_1, \mathbf{r}_2) \pm \psi(\mathbf{r}_2, \mathbf{r}_1) \end{aligned}$$

so that each combination of powers is included twice with different nonlinear parameters (i.e. a doubled basis set) gives a dramatic improvement in accuracy for basis sets of about the same total size [first introduced in the paper G.W.F. Drake, Phys. Rev. Lett. **59**, 1549 (1987)].

However, the optimization of the nonlinear parameters is now much more difficult, and an automated procedure is needed to find the minimum energy on a multidimensional energy surface.

The optimization can be efficiently done if derivatives of the energy w.r.t. the α 's and β 's are calculated. Starting from

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (15)$$

and assuming that $\langle \Psi | \Psi \rangle = 1$, then

$$\frac{\partial E}{\partial \alpha_t} = -2 \langle \Psi | H - E | r_1 \psi(\mathbf{r}_1, \mathbf{r}_2; \alpha_t) \pm r_2 \psi(\mathbf{r}_2, \mathbf{r}_1; \alpha_t) \rangle \quad (16)$$

where

$$\psi(\mathbf{r}_1, \mathbf{r}_2; \alpha_t) = \sum_{i,j,k} c_{ijk}^{(t)} \varphi_{ijk}(\alpha_t, \beta_t) \quad (17)$$

For example, Newton's method can be used to locate simultaneously the zeros of the first derivatives in an iterative procedure.

Homework Problems:

1. Prove the above equation for $\frac{\partial E}{\partial \alpha_t}$.
2. Prove that there is no contribution from the implicit dependence of $c_{ijk}^{(t)}$ on α_t if the linear parameters have been optimized.

THE SCREENED HYDROGENIC TERM

For Rydberg states, it is advantageous to include explicitly the screened hydrogenic term in the basis set, since for high L it gives correctly the first several figures in the energy. The screened hydrogenic energy is (in Z -scaled a.u.)

$$E_{\text{SH}} = -\frac{1}{2} \left[\frac{1}{n_1^2} + \left(\frac{Z-1}{Z} \right)^2 \frac{1}{n_2^2} \right] \quad (18)$$

so that

$$\begin{aligned} H - E_{\text{SH}} = & -\frac{1}{8} \left[\frac{A_1}{r_1^2} + \frac{B_1 + 8}{r_1} + \frac{C_1}{r^2} + D_1 + D_2 - \frac{4}{n_1^2} - \left(\frac{Z-1}{Z} \right)^2 \frac{4}{n_2^2} \right. \\ & \left. + \frac{A_2}{r_2} + \frac{B_2 + 8(Z-1)/Z}{r_2} + \frac{C_2}{r^2} \right] + Z^{-1} \left(\frac{1}{r} - \frac{1}{r_2} \right) \end{aligned}$$

This corresponds to writing the Hamiltonian in the form (in Z -scaled a.u.)

$$H = H_0(\mathbf{r}_1, Z) + H_0(\mathbf{r}_2, Z-1) + Z^{-1} \left(\frac{1}{r} - \frac{1}{r_2} \right) \quad (19)$$

with

$$H_0(\mathbf{r}_1, Z) = -\frac{1}{2} \nabla_1^2 - \frac{1}{r_1} \quad (20)$$

and

$$H_0(\mathbf{r}_2, Z-1) = -\frac{1}{2} \nabla_2^2 - \frac{Z-1}{Z} \frac{1}{r_2} \quad (21)$$

then the eigenvectors of $H_0 = H_0(\mathbf{r}_1, Z) + H_0(\mathbf{r}_2, Z - 1)$ are products of hydrogenic orbitals

$$\Psi_0 = \psi_0(1s, Z)\psi_0(nl, Z - 1) \quad (22)$$

and the eigenvalue is

$$E_{\text{SH}} = \left[-\frac{1}{2} - \left(\frac{Z-1}{Z} \right)^2 \frac{1}{2n^2} \right] Z^2 \text{ a.u.} \quad (23)$$

called the screened hydrogenic eigenvalue.

For high- L Rydberg states, E_{SH} and Ψ_0 are already excellent approximations. For example, for the $1s8d$ states, the energies are

$$\begin{aligned} E(1s8d \ ^1D) &= -2.007\,816\,512\,563\,81 \text{ a.u.} \\ E(1s8d \ ^3D) &= -2.007\,817\,934\,711\,71 \text{ a.u.} \\ E_{\text{SH}} &= -2.007\,812\,5 \text{ a.u.} \end{aligned}$$

It is therefore advantageous to include the screened hydrogenic terms in the basis set so that the complete trial function becomes

$$\Psi = c_0\Psi_0 + \sum_{ijk} \left[c_{ijk}^{(1)}\varphi_{ijk}(\alpha_1, \beta_1) + c_{ijk}^{(2)}\varphi(\alpha_2, \beta_2) \right] \pm \text{exchange} \quad (24)$$

Also, the variational principal can be re-expressed in the form

$$E = E_{\text{SH}} + \frac{\langle \Psi | H - E_{\text{SH}} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \quad (25)$$

so that the E_{SH} term can be cancelled analytically from the matrix elements, thereby avoiding numerical cancellation. For example

$$\langle \Psi_0 | H_0 - E_{\text{SH}} | \Psi_0 \rangle = 0 \quad (26)$$

and

$$\langle \varphi_{ijk} | H - E_{\text{SH}} | \Psi_0 \rangle = Z^{-1} \langle \varphi_{ijk} | \frac{1}{r} - \frac{1}{r_2} | \Psi_0 \rangle \quad (27)$$

There is also cancellation in the matrix elements themselves that can be removed to avoid numerical cancellation. Recall that

$$I_0(a, b, c) = \frac{2}{c+2} \sum_{i=0}^{[c+1]/2} \binom{c+2}{2i+1} [f(p, q; \beta) + f(p', q'; \alpha)] \quad (28)$$

where

$$f(p, q; x) = \frac{q!}{x^{q+1}(\alpha + \beta)^{p+1}} \sum_{j=0}^p \frac{(p+j)!}{j!} \left(\frac{x}{\alpha + \beta} \right)^j \quad (29)$$

where

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

If $\beta \ll \alpha$, then $f(p, q; \beta) \gg f(p', q'; \alpha)$ and the $j = 0$ term is the dominant contribution to $f(p, q; \beta)$. However, since this term depends only on the sum of powers $b + c$ for r_2 , it cancels exactly from the matrix element of $\frac{1}{r_{12}} - \frac{1}{r_2}$ and can therefore be omitted in the calculation of matrix elements, thereby saving many significant figures. This is especially valuable when $b + c$ is large and a is small.