

Special Topics on Precision Measurement in Atomic Physics: Lecture 3

Variational methods for helium and lithium

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organized by WIPM October 9 to November 13, 2019

TYPES OF CORRELATED HYLLERAAS BASIS SETS

Consider first the case of helium. In its simplest form, a Hylleraas wave function looks like

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{m=1}^N c_m \varphi_m$$

where m represents the m 'th combination of i, j, k and

$$\varphi_{ijk} = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1, l_2, L}^M(\hat{r}_1, \hat{r}_2) \pm \text{exchange}$$

The usual strategy is to include all triplets of powers such that $i + j + k \leq \Omega$. This defines a *Pekeris shell*, after Chaim Pekeris who did a great deal of work on helium calculations in the 1950s and 1960s. The objective is then to solve the generalized eigenvalue problem

$$\mathbf{H}\Psi = \lambda \mathbf{O}\Psi$$

where \mathbf{H} and \mathbf{O} are the Hamiltonian and overlap matrices respectively for this nonorthogonal basis set. The integer Ω is then progressively increased until the answer has converged to a sufficient degree of accuracy.

Problem: For Ω sufficiently large (about 18 in quadruple precision), the solution becomes numerically unstable due to round-off error and numerical linear dependence. This happens even in the one-electron case with a basis set of the simple form $r^n e^{-\alpha r}$ for $n \simeq 18$.

Solution: Double or triple the basis set by including each triplet of powers i, j, k more than once, but with different nonlinear parameters $\alpha^{(p)}$ and $\beta^{(p)}$. After optimization, the basis set then divides naturally into different sectors with different distance scales. The form is then

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{p=1}^{2 \text{ OR } 3} \sum_{m=1}^N c_m^{(p)} \varphi_m^{(p)}$$

where p labels the different sectors, and with

$$\varphi_{ijk}^{(p)} = r_1^i r_2^j r_{12}^k e^{-\alpha_p r_1 - \beta_p r_2} \mathcal{Y}_{l_1, l_2, L}^M(\hat{r}_1, \hat{r}_2) \pm \text{exchange}$$

In this way, the basis sets can be extended to much greater sizes and accuracy within the confines of ordinary quadruple-precision (about 32 decimal digit) arithmetic. The optimization of the α 's and β 's is deferred until later.

Other Types of Basis set

- **Molecular (γ)-basis set:** For molecules such as H_2^+ , the r_{12} coordinate plays the role of the internuclear coordinate, and so a special treatment is needed to model the vibrational part of the wave function with a γr_{12} term in the exponent. The molecular basis functions then have the form

$$\varphi_{ijk} = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \mathcal{Y}_{l_1, l_2, L}^M(\hat{r}_1, \hat{r}_2) \pm \text{exchange}$$

but with extra high powers of k such that $i + j \leq \Omega$ as usual, and k in the range $\Omega_{\text{low}} \leq k \leq \Omega_{\text{high}}$ with

$$\begin{aligned} \Omega_{\text{low}} &= N_p - \Omega + (i + j), \\ \Omega_{\text{high}} &= N_p + \Omega - (i + j). \end{aligned} \tag{1}$$

and $N_p \simeq 37$ [see M. M. Cassar and G. W. F. Drake, J. Phys. B, **37**, 2485 (2004)].

- **Random all-exponential basis set:** The basis functions have the purely exponential form

$$\varphi_p = e^{-\alpha_p r_1 - \beta_p r_2 - \gamma_p r_{12}} \mathcal{Y}_{l_1, l_2, L}^M(\hat{r}_1, \hat{r}_2) \pm \text{exchange}$$

with the $\alpha_p, \beta_p, \gamma_p$ chosen quasi-randomly from a few selected intervals [see V. I. Korobov, Phys. Rev. A **61**, 064503 (2000)]. Requires multiple-precision arithmetic due to numerical cancellation.

HYLLERAAS COORDINATES FOR LITHIUM There are now six coordinates $r_1, r_2, r_3, r_{12}, r_{23}, r_{31}$, and so the basis functions are

$$\varphi_{ijklmn} = \mathcal{A} r_1^i r_2^j r_3^k r_{12}^l r_{23}^m r_{31}^n e^{-\alpha r_1 - \beta r_2 - \gamma r_3} \mathcal{Y}_{l_1, l_2, l_3, L}^M(\hat{r}_1, \hat{r}_2, \hat{r}_3) \times (\text{spin function})$$

where \mathcal{A} is the antisymmetrization operator for doublet or quartet states. Include all terms such that $i + j + k + l + m + n \leq \Omega$. The basis set size grows as Ω^6 .

Early calculations were done by McKenzie and Drake [PRA **44**, 6973 (1991)] and greatly extended by Zong-Chao Yan and Li-Ming Wang, as will be discussed later, and also Krzysztof Pachucki, Mariusz Puchalski and co-workers in Poland.

VARIATIONAL BOUNDS

For any normalizable trial function Ψ_{tr} , the quantity

$$E_{\text{tr}} = \frac{\langle \Psi_{\text{tr}} | H | \Psi_{\text{tr}} \rangle}{\langle \Psi_{\text{tr}} | \Psi_{\text{tr}} \rangle}$$

is an upper bound to the true ground state energy (provided that the spectrum is bounded from below!).

PROOF

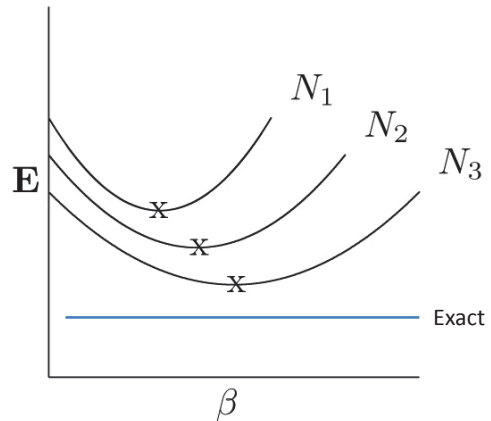
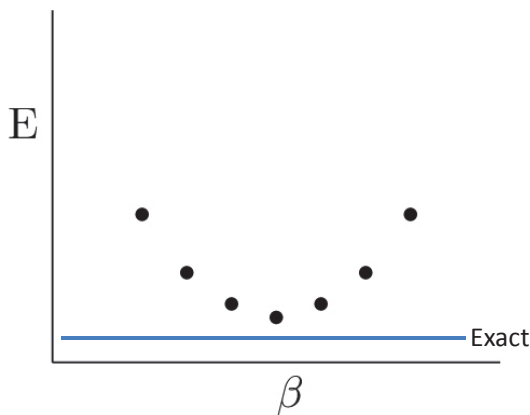
Even though the exact eigenfunctions ϕ_m of H are not known, they still exist in principle, and form a complete basis set (by assumption). It is therefore possible to expand (generalized Fourier series)

$$\Psi_{\text{tr}} = \sum_{m=0}^{\infty} a_m \phi_m$$

where, by assumption, $\langle \phi_m | \phi_n \rangle = \delta_{m,n}$, and $\langle \phi_m | H | \phi_n \rangle = \varepsilon_m \delta_{m,n}$. Also assume that $\langle \Psi_{\text{tr}} | \Psi_{\text{tr}} \rangle = 1$. Then, using $\sum_{m=0}^{\infty} |a_m|^2 = 1$, it follows that

$$\begin{aligned} E_{\text{tr}} &= \langle \Psi_{\text{tr}} | H | \Psi_{\text{tr}} \rangle \\ &= \sum_{m=0}^{\infty} |a_m|^2 \varepsilon_m \\ &= \varepsilon_0 + \sum_{m=1}^{\infty} |a_m|^2 (\varepsilon_m - \varepsilon_0) \end{aligned}$$

Thus $E_{\text{tr}} \geq \varepsilon_0$.



Hylleraas-Undheim-MacDonald Theorem

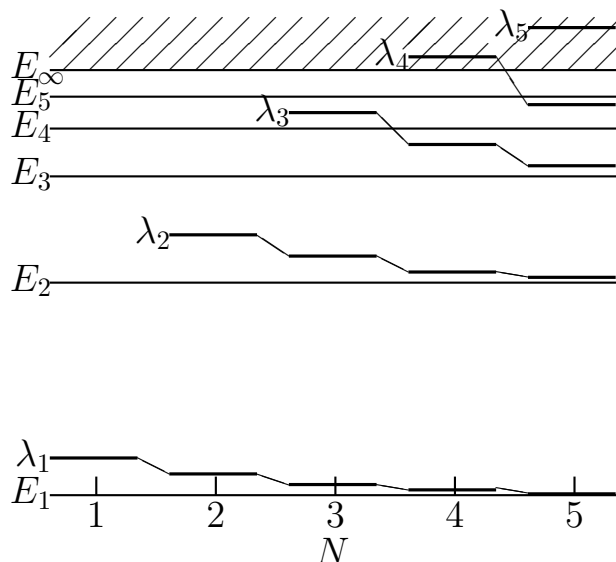


Diagram illustrating the Hylleraas-Undheim-MacDonald Theorem. The λ_p , $p = 1, \dots, N$ are the variational eigenvalues for an N -dimensional basis set, and the E_i are the exact eigenvalues of H . The highest λ_p lie in the continuous spectrum of H .

- According to the matrix interleaving theorem, each time a new basis function is added, the old eigenvalues interleave the new. Thus all the eigenvalues must move inexorably downward.
- It follows that all the eigenvalues are upper bounds to the exact energies, provided only that the correct number of eigenvalues lies lower. (This of course requires the spectrum to be bounded from below.)
No further orthogonalization is required.

References

1. E. A. Hylleraas and B. Undheim, Z. Phys. **65**, 759 (1930).
2. J. K. L. MacDonald, Phys. Rev. **43**, 830 (1933).

See also G. W. F. Drake *Variational Methods* in Encyclopedia of Applied Physics, Ed. by George L. Trigg (Wiley-VCH Verlag GmbH, 1998), Vol. 23, pp. 121–149 [reprinted in Mathematical Tools for Physicists, Ed. by George L. Trigg (Wiley-VCH Verlag GmbH & Co. KGaA, 2005), pp. 619-656].

SOLUTION OF THE EIGENVALUE PROBLEM

Recall how to diagonalize a 2×2 matrix

$$\begin{aligned} & \begin{pmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} H_{11} & H_{12} \\ H_{12} & H_{22} \end{pmatrix} \begin{pmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{pmatrix} \\ = & \begin{pmatrix} cH_{11} + sH_{12} & cH_{12} + sH_{22} \\ -sH_{11} + cH_{12} & -sH_{12} + cH_{22} \end{pmatrix} \begin{pmatrix} c & -s \\ s & c \end{pmatrix} \\ = & \begin{pmatrix} c^2H_{11} + s^2H_{22} + 2csH_{12} & (c^2 - s^2)H_{12} + cs(H_{22} - H_{11}) \\ (c^2 - s^2)H_{12} + cs(H_{22} - H_{11}) & s^2H_{11} + c^2H_{22} - 2csH_{12} \end{pmatrix} \end{aligned}$$

Therefore

$$(\cos^2 \theta - \sin^2 \theta)H_{12} = \cos \theta \sin \theta (H_{11} - H_{22})$$

and

$$\tan(2\theta) = \frac{2H_{12}}{H_{11} - H_{22}}$$

i.e.

$$\begin{aligned} \cos \theta &= \left(\frac{r + \omega}{2r} \right)^{1/2} \\ \sin \theta &= -\text{sgn}(H_{12}) \left(\frac{r - \omega}{2r} \right)^{1/2} \end{aligned}$$

where

$$\begin{aligned} \omega &= H_{22} - H_{11} \\ r &= (\omega^2 + 4H_{12}^2)^{1/2} \\ E_1 &= \frac{1}{2} (H_{11} + H_{22} - r) \\ E_2 &= \frac{1}{2} (H_{11} + H_{22} + r) \end{aligned}$$

Brute Force Method

Gives all the eigenvalues and eigenvectors, but it is slow. First orthonormalize the N -dimensional basis set; i.e. form linear combinations

$$\Phi_m = \sum_{n=1}^N \varphi_n R_{nm} \quad (2)$$

such that

$$\langle \Phi_m | \Phi_n \rangle = \delta_{m,n} \quad (3)$$

This can be done by finding an orthogonal transformation \mathbf{T} such that

$$\mathbf{T}^\top \mathbf{O} \mathbf{T} = \mathbf{I} = \begin{pmatrix} I_1 & 0 & 0 & \dots & 0 \\ 0 & I_2 & 0 & \dots & 0 \\ 0 & 0 & I_3 & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & I_N \end{pmatrix}; \quad (4)$$

$$O_{mn} = \langle \varphi_m | \varphi_n \rangle \quad (5)$$

and then applying a scale change matrix

$$\mathbf{S} = \begin{pmatrix} \frac{1}{I_1^{1/2}} & 0 & 0 & \dots & 0 \\ 0 & \frac{1}{I_2^{1/2}} & 0 & \dots & 0 \\ 0 & 0 & \frac{1}{I_3^{1/2}} & \dots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \dots & I_N^{1/2} \end{pmatrix} = \mathbf{S}^\top \quad (6)$$

Then

$$\mathbf{S}^\top \mathbf{T}^\top \mathbf{O} \mathbf{T} \mathbf{S} = \mathbf{1} \quad (7)$$

i.e.

$$\mathbf{R}^\top \mathbf{O} \mathbf{R} = \mathbf{1} \quad (8)$$

with $\mathbf{R} = \mathbf{T} \mathbf{S}$.

If \mathbf{H} is the matrix with elements $H_{mn} = \langle \varphi_m | \varphi_n \rangle$, then \mathbf{H} expressed in the Φ_m basis set is

$$\mathbf{H}' = \mathbf{R}^\top \mathbf{H} \mathbf{R}. \quad (9)$$

We next diagonalize \mathbf{H}' by finding an orthogonal transformation \mathbf{W} such that

$$\mathbf{W}^\top \mathbf{H}' \mathbf{W} = \boldsymbol{\lambda} = \begin{pmatrix} \lambda_1 & 0 & \dots & 0 \\ 0 & \lambda_2 & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \lambda_N \end{pmatrix} \quad (10)$$

where $\boldsymbol{\lambda}$ is the diagonal matrix of eigenvalues. The q 'th eigenvector is

$$\Psi^{(q)} = \sum_{n=1}^N \Phi_n W_{n,q} = \sum_{n,n'} \varphi_{n'} R_{n',n} W_{n,q} \quad (11)$$

i.e.

$$c_{n'}^{(q)} = \sum_{n=1}^N R_{n'n} W_{n,q} \quad (12)$$

The Power Method: is based on the observation that if \mathbf{H} has one eigenvalue λ_M that is much bigger than all the rest, and $\chi = \begin{pmatrix} a_1 \\ a_2 \\ \vdots \end{pmatrix}$ is an arbitrary starting vector, then it is always possible to express χ as a linear combination of the true eigenvectors $\Psi^{(q)}$ in the form $\chi = \sum_{q=1}^N x_q \Psi^{(q)}$.

$$(\mathbf{H})^n \chi = \sum_{q=1}^N x_q \lambda_q^n \Psi^{(q)} \rightarrow x_M \lambda_M^n \Psi^{(M)} \quad (13)$$

provided $x_M \neq 0$.

To pick out the eigenvector corresponding to any eigenvalue, write the original problem in the form

$$\begin{aligned} \mathbf{H}\Psi &= \lambda\mathbf{O}\Psi \\ (\mathbf{H} - \lambda_q\mathbf{O})\Psi &= (\lambda - \lambda_q)\mathbf{O}\Psi \end{aligned}$$

Therefore,

$$\mathbf{G}\Psi = \frac{1}{\lambda - \lambda_q} \Psi \quad (14)$$

where $\mathbf{G} = (\mathbf{H} - \lambda_q\mathbf{O})^{-1}\mathbf{O}$ with eigenvalues $\frac{1}{\lambda_n - \lambda_q}$.

By picking λ_q close to any one of the λ_n , say $\lambda_{n'}$, then $\frac{1}{\lambda_n - \lambda_q}$ is much larger for $n = n'$ than for any other value. The sequence is then

$$\begin{aligned} \chi_1 &= \mathbf{G}\chi \\ \chi_2 &= \mathbf{G}\chi_1 \\ \chi_3 &= \mathbf{G}\chi_2 \\ &\vdots \end{aligned}$$

until the ratios of components in χ_n stop changing.

Useful Trick: To avoid matrix inversion and multiplication, note that the sequence is equivalent to

$$\mathbf{F}\chi_n = (\lambda - \lambda_q)\mathbf{O}\chi_{n-1} \quad (15)$$

where $\mathbf{F} = \mathbf{H} - \lambda_q\mathbf{O}$. The factor of $(\lambda - \lambda_q)$ can be dropped because this only affects the normalization of χ_n . To find χ_n , solve

$$\mathbf{F}\chi_n = \mathbf{O}\chi_{n-1} \quad (16)$$

(N equations in N unknowns). Then

$$\lambda = \frac{\langle \chi_n | H | \chi_n \rangle}{\langle \chi_n | \chi_n \rangle} \quad (17)$$