Special Topics on Precision Measurement in Atomic Physics: Lecture 2

Overview of theoretical techniques (H.F, C.I., MBPT, Hylleraas)

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Sponsored by USTC, organized by WIPM
October 9 to November 13, 2019

METHODS OF THEORETICAL ATOMIC PHYSICS

For systems more complicate than hydrogen, exact analytic solutions are not possible, and so approximation methods must be used.

Methods of Theoretical Atomic Physics.

Method	Typical Accuracy for the Energy
Many Body Perturbation Theory	$\geq 10^{-6}$ a.u.
Configuration Interaction	$10^{-6} - 10^{-8}$ a.u.
Explicitly Correlated Gaussians[a]	$\sim 10^{-10}$ a.u.
Hylleraas Coordinates (He)[b,c,d]	$\leq 10^{-35} - 10^{-40}$ a.u.
Hylleraas Coordinates (Li)[e,f]	$\sim 10^{-15}$ a.u.

[a]S. Bubin and Adamowicz J. Chem. Phys. **136**, 134305 (2012).

[b]C. Schwartz, Int. J. Mod. Phys. E–Nucl. Phys. **15**, 877 (2006).

[c]H. Nakashima, H. Nakatsuji, J. Chem. Phys. **127**, 224104 (2007).

[d]D.T. Aznabaev et al., Phys. Rev. A **98**, 012510 (2018).

[e] M. Puchalski et al. Phys. Rev. A **87** 030502 (2017).
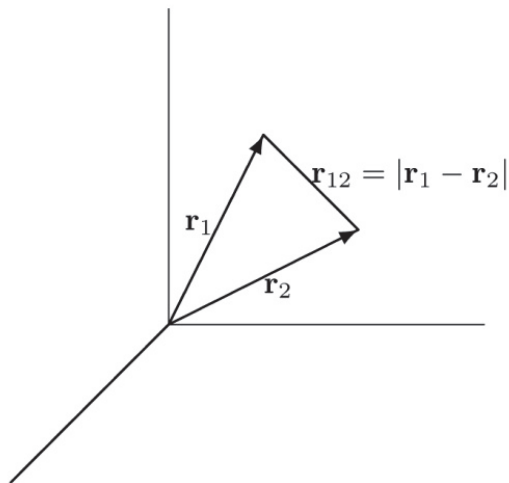
[f] L.M. Wang et al., Phys. Rev. A **95**, R032504 (2017).

Z-SCALED ATOMIC UNITS

The starting point is the two-electron Schrödinger equation for infinite nuclear mass

$$\left[-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{r_{12}} \right] \psi = E\psi$$

where m is the electron mass, and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ (see diagram below).

Begin by rescaling distances and energies so that the Schrödinger equation can be expressed in a dimensionless form. The dimensionless Z-scaled distance is defined by

$$\rho = \frac{Zr}{a_0}$$

where

$$a_0 = \frac{\hbar^2}{me^2}$$

is the atomic unit (a.u.) of distance equal to the Bohr radius $0.529\,177\,210\,903(80) \times 10^{-10}$ m. Then

$$[-\frac{\hbar^2}{2m}Z^2\left(\frac{me^2}{\hbar^2}\right)^2(\nabla^2_{\rho_1} + \nabla^2_{\rho_2}) - Z^2\frac{e^2}{a_0}\rho_1^{-1} - Z^2\frac{e^2}{a_0}\rho_2^{-1} + \frac{e^2}{a_0}Z\rho_{12}^{-1}]\psi = E\psi$$

But

$$\frac{\hbar^2}{m}\left(\frac{me^2}{\hbar^2}\right)^2 = \frac{e^2}{a_0}$$

is the hartree atomic unit of of energy ($E_h = 27.211386\,245\,988(53)$ eV, or equivalently $E_h/(hc) = 219\,474.631\,363\,20(43)$ cm^{-1}). Therefore, after multi-

plying through by $a_0/(Ze)^2$, the problem to be solved in Z-scaled dimension-less units becomes

$$[-\frac{1}{2}(\nabla^2_{\rho_1} + \nabla^2_{\rho_2}) - \frac{1}{\rho_1} - \frac{1}{\rho_2} + \frac{Z^{-1}}{\rho_{12}}]\psi = \varepsilon\psi$$

where

$$\varepsilon = \frac{Ea_0}{(Ze)^2}$$

is the energy in Z-scaled atomic units. For convenience, rewrite this in the conventional form

$$H\psi = \varepsilon\psi$$

where (using r in place of ρ for the Z-scaled distance)

$$H = -\frac{1}{2}(\nabla^2_1 + \nabla^2_2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{Z^{-1}}{r_{12}}$$

is the atomic Hamiltonian for infinite nuclear mass.

THE HARTREE-FOCK METHOD

For purposes of comparison, and to define the correlation energy, assume that $\psi(\mathbf{r}_1, \mathbf{r}_2)$ can be written in the separable product form

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[u_1(r_1)u_2(r_2) \pm u_2(r_1)u_1(r_2)]$$

for the $1s^2\ {}^1S$ ground state. Because of the $\frac{1}{r_{12}}$ term in the Schrödinger equation, the exact solution cannot be expressed in this form as a separable product. However, the Hartree-Fock (or Dirac-Fock) approximation corresponds to finding the best possible solution to the Schrödinger (or Dirac) equation

$$H\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2)$$

that can nevertheless be expressed in this separable product form, where as before

$$H = -\frac{1}{2}(\nabla^2_1 + \nabla^2_2) - \frac{1}{r_1} - \frac{1}{r_2} + \frac{Z^{-1}}{r_{12}}$$

is the full two-electron Hamiltonian. To find the best solution, substitute into $\langle \psi \mid H - E \mid \psi \rangle$ and require this expression to be stationary with respect to

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arbitrary infinitesimal variations δu_1 and δu_2 in u_1 and u_2 respectively; i.e.

$$\frac{1}{2}\langle \delta u_1(r_1)u_2(r_2) \pm u_2(r_1)\delta u_1(r_2) \mid H - E \mid u_1(r_1)u_2(r_2) \pm u_2(r_1)u_1(r_2) \rangle$$

$$= \int \delta u_1(r_1)\, d\mathbf{r}_1 \left\{ \int d\mathbf{r}_2\, u_2(r_2)\,(H-E)\,[u_1(r_1)u_2(r_2) \pm u_2(r_1)u_1(r_2)] \right\}$$

$$= 0$$

for arbitrary $\delta u_1(r_1)$. Therefore $\{\int d\mathbf{r}_2 \ldots\} = 0$.

Similarly, the coefficient of δu_2 would give

$$\int d\mathbf{r}_1\, u_1(r_1)\,(H-E)\,[u_1(r_1)u_2(r_2) \pm u_2(r_1)u_1(r_2)] = 0$$

Define

$$I_{12} = I_{21} = \int d\mathbf{r}\, u_1(r)u_2(r),$$

$$H_{ij} = \int d\mathbf{r}\, u_i(r)(-\frac{1}{2}\nabla - \frac{1}{r})u_j(r),$$

$$G_{ij}(r) = \int d\mathbf{r}'\, u_i(r')\frac{1}{|\mathbf{r} - \mathbf{r}'|}u_j(r')$$

Then the above equations become the pair of integro-differential equations

$$[H_0 - E + H_{22} + G_{22}(r)]u_1(r) = \mp[I_{12}(H_0 - E) + H_{12} + G_{12}(r)]u_2(r)$$
$$[H_0 - E + H_{11} + G_{11}(r)]u_2(r) = \mp[I_{12}(H_0 - E) + H_{12} + G_{12}(r)]u_1(r)$$

These must be solved self-consistently for the "constants" I_{12} and H_{ij} and the function $G_{ij}(r)$.

The Hartree Fock energy is $E \simeq -2.87\ldots$ a.u. while the exact energy is $E = -2.903\,724\ldots$ a.u. The difference is called the "correlation energy" because it arises from the way in which the motion of one electron is correlated to the other. The Hartree-Fock equations only describe how one electron moves in the average field provided by the other (mean-field theory).

CONFIGURATION INTERACTION

Expand

$$
\begin{aligned}
\psi(\mathbf{r}_1, \mathbf{r}_2) &= C_0 u_1^{(s)}(r_1) u_1^{(s)}(r_2) + C_1 u_1^{(P)}(\mathbf{r}_1) u_1^{(P)}(\mathbf{r}_2) \mathcal{Y}_{1,1,0}^0(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \\
&+ C_2 u_1^{(d)}(\mathbf{r}_1) u_2^{(d)}(\mathbf{r}_2) \mathcal{Y}_{2,2,0}^0(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) + ... \pm \text{ exchange}
\end{aligned}
$$

where

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

This works, but is slowly convergent, and very laborious. The best CI calculations are accurate to $\sim 10^{-7}$ a.u.

PERTURBATION THEORY

In the standard way, write

$$
H = H_0 + \lambda V_1
$$

where λ is a perturbation parameter and, for example, $V_1 = V_{\text{exact}} - V_{\text{HF}}$. Expand

$$
\begin{aligned}
\Psi &= \Psi_0 + \lambda \Psi_1 + \cdots \\
E &= E_0 + \lambda E_1 + \cdots
\end{aligned}
$$

Substitute into $H\Psi = E\Psi$ and collect equal powers of λ to obtain

$$
\begin{aligned}
\lambda^0 : \quad & (H_0 - E_0)\Psi_0 = 0 \\
\lambda^1 : \quad & (H_0 - E_0)\Psi_1 + V_1 \Psi_0 = E_1 \Psi_0 \\
\lambda^2 : \quad & (H_0 - E_0)\Psi_2 + V_1 \Psi_1 = E_1 \Psi_1 + E_2 \Psi_0
\end{aligned}
$$

The energy expansion coefficients up to second-order are then

$$
E_1 = \langle \Psi_0 \mid V_1 \mid \Psi_0 \rangle \tag{1}
$$

and

$$
E_2 = \sum_{n \neq 0}^{\infty} \frac{\langle \Psi_0 \mid V_1 \mid \Psi_n \rangle \langle \Psi_n \mid V_1 \mid \Psi_0 \rangle}{E_0 - E_n} \tag{2}
$$

including an integration over the continuum. For a many-electron atom, express in terms of Slater determinants, or second quantization formalism. Accuracy is limited to a few parts in 10^6. Later on in the course, we will use the method of Dalgarno and Lewis and/or pseudostates to perform the infinite summations.

HYLLERAAS COORDINATES

[E.A. Hylleraas, Z. Phys. **48**, 469 (1928) and **54**, 347 (1929) suggested using the co-ordinates r_1, r_2 and $r_{12} =\mid \mathbf{r}_1 - \mathbf{r}_2 \mid$, or equivalently

$$
\begin{aligned}
s &= r_1 + r_2, \\
t &= r_1 - r_2, \\
u &= r_{12}
\end{aligned}
$$

and writing the trial functions in the form

$$
\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i,j,k}^{i+j+k \leq N} c_{i,j,k} r_1^{i+l_1} r_2^{j+l_2} r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1,l_2,L}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \pm \text{exchange}
$$

where

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

is a vector-coupled product of spherical harmonics to form a state of total angular momentum L and z-component M. Diagonalizing H in this nonorthogonal basis set is equivalent to solving

$$
\frac{\partial E}{\partial c_{i,j,k}} = 0
$$

for fixed α and β.

The diagonalization must be repeated for different values of α and β in order to optimize the nonlinear parameters.

COMPLETENESS

The completeness of the above basis set can be shown by first writing

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

and, from the spherical harmonic addition theorem,

$$\cos(\theta_{12}) = \frac{4\pi}{3} \sum_{m=-1}^{1} Y_1^{m*}(\theta_1, \varphi_1) Y_1^m(\theta_2, \varphi_2)$$

Consider first the S-states. The r_{12}^0 terms are like the ss' terms in a CI calculation. The r_{12}^2 terms bring in pp type contributions, and the higher powers bring in dd, ff etc. type terms. In general

$$P_l(\cos\theta_{12}) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_l^{m*}(\theta_1, \varphi_1) Y_l^m(\theta_2, \varphi_2)$$

For P-states, one would have similarly

$$\begin{aligned}
r_{12}^0 &\rightarrow (sp)P \\
r_{12}^2 &\rightarrow (pd)P \\
r_{12}^4 &\rightarrow (df)P \\
&\vdots \qquad \vdots
\end{aligned}$$

For D-states

$$\begin{aligned}
r_{12}^0 &\rightarrow (sd)D \quad (pp')D \\
r_{12}^2 &\rightarrow (pf)D \quad (dd')D \\
r_{12}^4 &\rightarrow (dg)D \quad (ff')D \\
&\vdots \qquad\quad \vdots \qquad\quad \vdots
\end{aligned}$$

In this case, since there are two "lowest-order" couplings to form a D-state, both must be present in the basis set, i.e.

$$\begin{aligned}
\Psi(r_2, r_2) &= \sum c_{ijk} r_1^i r_2^{j+2} r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{022}^M(\hat{r}_1, \hat{r}_2) \\
&+ \sum d_{ijk} r_1^{i+1} r_2^{j+1} r_{12}^k e^{-\alpha' r_1 - \beta' r_2} \mathcal{Y}_{112}^M(\hat{r}_1, \hat{r}_2)
\end{aligned}$$

For F-states, one would need $(sf)F$ and $(pd)F$ terms.

For G-states, one would need $(sg)G$, $(pf)G$ and $(dd')G$ terms.

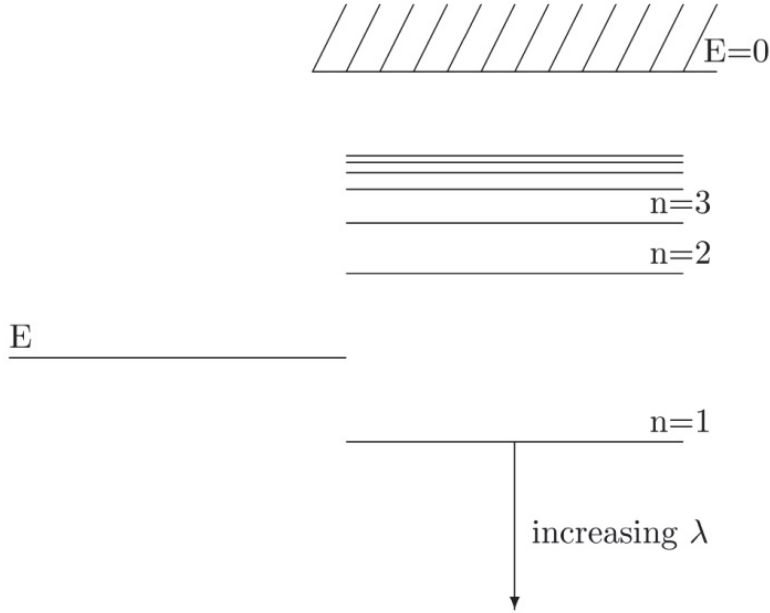Completeness of the radial functions can be proven by considering the Sturm-Liouville problem

$$\left(-\frac{1}{2}\nabla^2 - \frac{\lambda}{r_s} - E \right) \psi(\mathbf{r}) = 0$$

or

$$\left(-\frac{1}{2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \frac{l\left(l+1\right)}{2r^2} - \frac{\lambda}{r} - E\right) u(r) = 0.$$

For fixed E and variable λ (nuclear charge).

The eigenvalues are $\lambda_n = (E/E_n)^{1/2}$, where $E_n = -\frac{1}{2n^2}$.

and the eigenfunctions are

$$u_{nl}(r) \;=\; \frac{1}{(2l+1)!}\left(\frac{(n+l)!}{(n-l-1)2!}\right)^{1/2}(2\alpha)^{3/2}e^{-\alpha r}$$
$$\times\; (2\alpha r)^l \,{}_1F_1\left(-n+l+1, 2l+2; 2\alpha r\right)$$

with $\alpha = (-2E)^{1/2}$ and $n \geq l+1$. The confluent hypergeometric function ${}_1F_1(a, b, ; z)$ then denotes a finite polynomial since $a = -n+l+1$ is a negative integer or zero.

Unlike the hydrogen spectrum, which has both a discrete part for $E < 0$ and a continuous part for $E > 0$, this forms an entirely discrete set of finite

polynomials, called Sturmian functions. They are orthogonal with respect to the potential, i.e.

$$\int_0^\infty r^2 dr \left(u_{n'l}(r) \frac{1}{r} u_{nl}(r) \right) = \delta_{n,n'}$$

Since they become complete in the limit $n \to \infty$, this assures the completeness of the variational basis set.

[See also B Klahn and W.A. Bingel Theo. Chim. Acta (Berlin) **44**, 9 and 27 (1977)].

SPECIAL ROLE OF ODD POWERS OF r_{12}

The above shows that the Hylleraas basis set is complete with just the even powers of r_{12}, and at this level it is equivalent to CI. But it is the *odd* powers that greatly accelerate the rate of convergence because they reproduce the electron-electron cusp at $r_{12} = 0$.

Energies for the ground state of helium
obtained with various powers of r_{12} in the basis set.

r_{12} terms [a]	Energy (a.u.)	Error (eV)
no r_{12}	−2.879 024	0.672
r_{12}^2	−2.900 503	0.087 6
r_{12}^2, r_{12}^4	−2.902 752	0.026 4
r_{12}	−2.903 496	0.006 20
r_{12}, r_{12}^3	−2.903 700	0.000 65
all r_{12}	−2.903 724	0.000 00

[a] Includes all powers of r_1 and r_2.

HOMEWORK

Consider the matrix eigenvalue problem described by the 2×2 matrix

$$\mathbf{H} = \begin{pmatrix} E_0 & \lambda V \\ \lambda V & E_1 \end{pmatrix}$$

where E_0 and E_1 are the unperturbed eigenvalues, and λV is a perturbation. Find the exact lowest eigenvalue $E(\lambda)$ as a function of the perturbation parameter λ and show that a power series expansion of $E(\lambda)$ agrees with the

results of the perturbation equations (1) and (2) up to terms of order λ^2. In this case, the spectrum has only two states and so the summation in Eq. (2) has only one term corresponding to $n = 1$. The lesson to be learned is that summing the perturbation series is equivalent to exact matrix diagonalization.