

# Special Topics on Precision Measurement in Atomic Physics: Lecture 9

## Applications to states of high angular momentum

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We have already seen that a simple structure emerges for states of high angular momentum.

Variational energies for the  $n = 10$  singlet and triplet states of helium.

State	Singlet	Triplet
10 S	-2.005 142 991 747 919(79)	-2.005 310 794 915 611 3(11)
10 P	-2.004 987 983 802 217 9(26)	-2.005 068 805 497 706 7(30)
10 D	-2.005 002 071 654 256 81(75)	-2.005 002 818 080 228 84(53)
10 F	-2.005 000 417 564 668 80(11)	-2.005 000 421 686 604 88(26)
10 G	-2.005 000 112 764 318 746(22)	-2.005 000 112 777 003 317(21)
10 H	-2.005 000 039 214 394 532(17)	-2.005 000 039 214 417 416(17)
10 I	-2.005 000 016 086 516 1947(3)	-2.005 000 016 086 516 2194(3)
10 K	-2.005 000 007 388 375 8769(0)	-2.005 000 007 388 375 8769(0)

$-2.005\,000\dots$  is the screened hydrogenic eigenvalue  $E_{\text{SH}} = -2 - 1/(2n^2)$  with  $n = 10$ . Note that for the  $K$ -states, the difference between the singlet and triplet energy is no longer visible. The correction to  $E_{\text{SH}}$  is then fully accounted for by a core-polarization model.

## ASYMPTOTIC EXPANSIONS

### Core Polarization Model (A. Dalgarno, R. Drachman)

- neglect exchange.
- Rydberg electron moves in the field generated by the polarizable core.

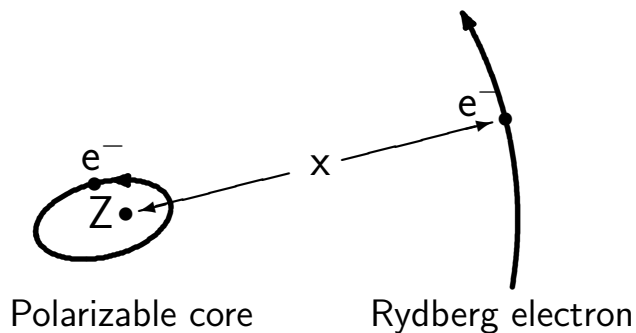


Illustration of the physical basis for the asymptotic expansion method in which the Rydberg electron moves in the field generated by the polarized core.

$$V(x) = -\frac{Z-1}{x} + \Delta V(x)$$

$$\Delta V(x) = -\frac{c_4}{x^4} - \frac{c_6}{x^6} - \frac{c_7}{x^7} - \frac{c_8}{x^8} - \frac{c_9}{x^9} - \frac{c_{10}}{x^{10}} + \dots$$

For example,  $c_4 = \frac{1}{2}\alpha_1$

$$c_6 = \frac{1}{2}(\alpha_2 - 6\beta_1)$$

$$\alpha_1 = \frac{9}{2Z^4} \text{ is the dipole polarizability,}$$

$$\alpha_2 = \frac{15}{Z^6} \text{ is the quadrupole polarizability,}$$

$$\beta_1 = \frac{43}{8Z^6} \text{ is a nonadiabatic correction.}$$

## §10.17(i) Hankel's Expansions



Define  $a_0(\nu) = 1$ ,

### Asymptotic expansions of Bessel functions

10.17.1

$$a_k(\nu) = \frac{(4\nu^2 - 1^2)(4\nu^2 - 3^2) \cdots (4\nu^2 - (2k - 1)^2)}{k! 8^k},$$

$k \geq 1$ ,

10.17.2

$$\omega = z - \frac{1}{2} \nu \pi - \frac{1}{4} \pi,$$



and let  $\delta$  denote an arbitrary small positive constant. Then as  $z \rightarrow \infty$ , with  $\nu$  fixed,

10.17.3

$$J_\nu(z) \sim \left(\frac{2}{\pi z}\right)^{\frac{1}{2}} \left( \cos \omega \sum_{k=0}^{\infty} (-1)^k \frac{a_{2k}(\nu)}{z^{2k}} - \sin \omega \sum_{k=0}^{\infty} (-1)^k \frac{a_{2k+1}(\nu)}{z^{2k+1}} \right),$$

$|\text{ph } z| \leq \pi - \delta$ ,

10.17.4

$$Y_\nu(z) \sim \left(\frac{2}{\pi z}\right)^{\frac{1}{2}} \left( \sin \omega \sum_{k=0}^{\infty} (-1)^k \frac{a_{2k}(\nu)}{z^{2k}} + \cos \omega \sum_{k=0}^{\infty} (-1)^k \frac{a_{2k+1}(\nu)}{z^{2k+1}} \right),$$

$|\text{ph } z| \leq \pi - \delta$ ,

10.17.5

$$H_\nu^{(1)}(z) \sim \left(\frac{2}{\pi z}\right)^{\frac{1}{2}} e^{i\omega} \sum_{k=0}^{\infty} i^k \frac{a_k(\nu)}{z^k},$$

$-\pi + \delta \leq \text{ph } z \leq 2\pi - \delta$ ,

10.17.6

$$H_\nu^{(2)}(z) \sim \left(\frac{2}{\pi z}\right)^{\frac{1}{2}} e^{-i\omega} \sum_{k=0}^{\infty} (-i)^k \frac{a_k(\nu)}{z^k},$$

$-2\pi + \delta \leq \text{ph } z \leq \pi - \delta$ ,

From <https://dlmf.nist.gov/10.17>

Then

$$\Delta E_{nL} = -\frac{(Z-1)^2}{2n^2} + \langle \chi_0 | \Delta V(x) | \chi_0 \rangle + \langle \chi_0 | \Delta V(x) | \chi_1 \rangle$$

where  $|\chi_0\rangle =$  unperturbed wave function for the Rydberg electron, and  $|\chi_1\rangle =$  first-order perturbation correction to  $|\chi_0\rangle$  due to  $\Delta V(x)$ ; i.e.

$$[h_0(x) - e_0] |\chi_1\rangle + \Delta V(x) |\chi_0\rangle = |\chi_0\rangle \langle \chi_0 | \Delta V(x) | \chi_0 \rangle$$

All calculations can be done analytically, using methods of Dalgarno and Stewart (1956-60) and Cohen and Dalgarno (1961-66), especially the “Dalgarno Interchange Theorem.”

See G.W.F. Drake, *Adv. At. Mol. Opt. Phys.* **31**, 1 (1993).

## MATHEMATICAL FORMULATION

(See G.W.F. Drake, Adv. At. Mol. Opt. Phys. **31**, 1(1993). Treat the inner and outer electrons as *distinguishable* particles and ignore exchange. We can then write the Hamiltonian in the form

$$H = \underbrace{-\frac{1}{2}\nabla_r^2 - \frac{Z}{r}}_{h_0(r, Z)} \underbrace{-\frac{1}{2}\nabla_x^2 - \frac{Z-1}{x}}_{h_0(x, Z-1)} + \underbrace{\left(\frac{1}{|\mathbf{r}-\mathbf{x}|} - \frac{1}{x}\right)}_{\Delta V(\mathbf{r}, \mathbf{x})} \quad (1)$$

Assume that  $x \gg r$  and expand

$$\Delta V(\mathbf{r}, \mathbf{x}) = \frac{1}{|\mathbf{r}-\mathbf{x}|} - \frac{1}{x} = \sum_{l=1}^{\infty} \frac{r^l}{x^{l+1}} P_l(\hat{\mathbf{r}} \cdot \hat{\mathbf{x}}) \quad (2)$$

Note that the  $l = 0$  term cancels. Consider first the  $l = 1$  term as a small perturbation. Then  $\Delta V = r \cos \theta / x^2$ . The unperturbed problem is

$$[h_0(r, Z) + h_0(x, Z-1) - E_{\text{SH}}]\Psi(r, x) = 0 \quad (3)$$

where  $\Psi(r, x)$  has the separable product form

$$\Psi(r, x) = \varphi_{1s}(r)\chi_{nl}(x) \quad (4)$$

The first-order energy vanishes, and second-order energy is

$$\Delta E_2 = \sum_{K,k} \frac{\langle \varphi_{1s}(r)\chi_{nl}(x) | \frac{r \cos \theta}{x^2} | \varphi_K(r)\chi_k(x) \rangle \langle \varphi_K(r)\chi_k(x) | \frac{r \cos \theta}{x^2} | \varphi_{1s}(r)\chi_{nl}(x) \rangle}{D_K + d_k} \quad (5)$$

where

$$\begin{aligned} D_K &= E_{1s} - E_K \\ d_k &= e_{nl} - e_k \end{aligned}$$

Now expand the denominator as a power series

$$\frac{1}{D_K + d_k} = \frac{1}{D_K} \left[ 1 - \frac{d_k}{D_K} + \left(\frac{d_k}{D_K}\right)^2 + \dots \right] \quad (6)$$

The leading term gives

$$\Delta E_2 = \sum_{K,k} \frac{\langle \varphi_{1s}(r) \chi_{nl}(x) | \frac{r \cos \theta}{x^2} | \varphi_K(r) \chi_k(x) \rangle \langle \varphi_K(r) \chi_k(x) | \frac{r \cos \theta}{x^2} | \varphi_{1s}(r) \chi_{nl}(x) \rangle}{D_K} \quad (7)$$

Since the integrals over  $r$  and  $x$  are independent, and  $d_k$  no longer appears in the denominator, we can complete the sum over  $k$  by closure

$$\sum_k | \chi_k \rangle \langle \chi_k | = 1$$

and regroup the terms in the form

$$\begin{aligned} \Delta E_2 &= \langle \chi_{nl} | \frac{1}{x^4} | \chi_{nl} \rangle \sum_K \frac{\langle \varphi_{1s} | r \cos \theta | \varphi_K \rangle \langle \varphi_K | r \cos \theta | \varphi_{1s} \rangle}{D_K} \\ &= -\frac{\alpha_1}{2} \langle \chi_{nl} | \frac{1}{x^4} | \chi_{nl} \rangle \end{aligned} \quad (8)$$

where

$$\alpha_1 = -2 \sum_K \frac{\langle \varphi_{1s} | r \cos \theta | \varphi_K \rangle \langle \varphi_K | r \cos \theta | \varphi_{1s} \rangle}{D_K} \quad (9)$$

is the dipole polarizability.

### Perturbation Calculation of $\alpha_1$

$\alpha_1$  can be calculated exactly by solving the perturbation equation for hydrogenlike  $\text{He}^+$  (see problem)

$$(h_0 - E_0)\varphi^{(1)} + r \cos \theta \varphi_{1s}^{(0)} = 0 \quad (10)$$

Then

$$\begin{aligned} \alpha_1 &= 2 \langle \varphi^{(1)} | r \cos \theta | \varphi_{1s}^{(0)} \rangle \\ &= \frac{9}{2Z^4} \end{aligned} \quad (11)$$

Also, for the expectation value of  $1/x^4$

$$\langle x^{-4} \rangle = \frac{16[3n^2 - l(l+1)]}{n^5(2l+3)(2l+2)(2l+1)(2l)(2l-1)} \quad (12)$$

The total is thus

$$\Delta E_2 = -\frac{1}{2} \left( \frac{9}{32} \right) \frac{16(300 - 7 \cdot 8)}{17 \cdot 16 \cdot 15 \cdot 14 \cdot 13} \quad (13)$$

This gives  $\Delta E_2 = -\frac{183}{24752000000} = -0.000\,000\,007\,393\,341\,95 \dots$

Higher values of  $l$  in  $\Delta V$  give quadrupole, octupole, ... corrections. This is called the *adiabatic approximation*.

### Asymptotic expansion for the energy of the 1s10k state of helium

Quantity	Value
$-Z^2/2$	-2.000 000 000 000 000 00
$-1/(2n^2)$	-0.005 000 000 000 000 00
$c_4 \langle r^{-4} \rangle$	-0.000 000 007 393 341 95
Total	-2.005 000 007 393 341 95
Variational	-2.005 000 007 388 375 8769(0)
Difference	-0.000 000 000 004 966 08
	$\simeq 33$ kHz

## Nonadiabatic Corrections

The next term in the expansion

$$\frac{1}{D_K + d_k} = \frac{1}{D_K} \left[ 1 - \frac{d_k}{D_K} + \left( \frac{d_k}{D_K} \right)^2 + \dots \right] \quad (14)$$

i.e.  $-\frac{d_k}{D_K}$  gives the leading nonadiabatic correction. The contribution to the second-order energy is

$$\Delta E_2^{(1)} = \sum_{K,k} \frac{d_k \langle \varphi_{1s}(r) \chi_{nl}(x) \mid \frac{r \cos \theta}{x^2} \mid \varphi_K(r) \chi_k(x) \rangle \langle \varphi_K(r) \chi_k(x) \mid \frac{r \cos \theta}{x^2} \mid \langle \varphi_{1s}(r) \chi_{nl}(x) \rangle}{D_K^2} \quad (15)$$

The trick now is to replace  $d_k = e_{nl} - e_k$  by the operator  $e_{nl} - h(x)$  inside the matrix element so that the numerator  $\mathcal{N}_{k,K}$  summed over  $k$  becomes

$$\begin{aligned} \sum_k \mathcal{N}_{k,K} &= \sum_k \langle \varphi_{1s}(r) \chi_{nl}(x) | \frac{r \cos \theta}{x^2} | [e_{nl} - h(x)] \varphi_K(r) \chi_k(x) \rangle \\ &\quad \times \langle \varphi_K(r) \chi_k(x) | \frac{r \cos \theta}{x^2} | \langle \varphi_{1s}(r) \chi_{nl}(x) \rangle \end{aligned} \quad (16)$$

Once again the sum over  $k$  can be completed by closure, and the matrix elements factored into independent parts to obtain

$$\begin{aligned} \sum_k \mathcal{N}_{k,K} &= \langle \varphi_{1s}(r) | r \cos \theta | \varphi_K(r) \rangle \langle \varphi_K(r) | r \cos \theta | \varphi_{1s}(r) \rangle \\ &\quad \times \langle \chi_{nl}(x) | \frac{1}{x^2} [e_{nl} - h(x)] \frac{1}{x^2} | \chi_{nl}(x) \rangle \end{aligned} \quad (17)$$

Next commute the operator  $e_{nl} - h(x)$  through to the right and use

$$[e_{nl} - h(x)] | \chi_{nl} \rangle = 0$$

to obtain the remaining part  $\langle \chi_{nl}(x) | x^{-2} (\nabla x^{-2}) \cdot \nabla | \chi_{nl}(x) \rangle$ . An integration by parts then yields the final result for the matrix element

$$\begin{aligned} \langle \chi_{nl}(x) | x^{-2} (\nabla x^{-2}) \cdot \nabla | \chi_{nl}(x) | \chi_{nl}(x) \rangle &= \frac{1}{4} \langle \chi_{nl}(x) | (\nabla^2 x^{-4}) | \chi_{nl}(x) \rangle \\ &= 3 \langle \chi_{nl}(x) | x^{-6} | \chi_{nl}(x) \rangle \end{aligned} \quad (18)$$

The final result for the leading nonadiabatic correction is thus

$$\Delta E_2^{(1)} = \frac{\beta_1}{3} \beta_1 \langle \chi_{nl} | x^{-6} | \chi_{nl} \rangle \quad (19)$$

with

$$\begin{aligned} \beta_1 &= \sum_K \frac{\langle \varphi_{1s}(r) | r \cos \theta | \varphi_K(r) \rangle \langle \varphi_K(r) | r \cos \theta | \varphi_{1s}(r) \rangle}{D_K^2} \\ &= \frac{43}{8Z^6} \end{aligned} \quad (20)$$



Values of the asymptotic expansion coefficients. The quantities  $\beta_l$ , and  $\gamma_l$ , and  $\delta_l$  are respectively first, second and third nonadiabatic corections to the multipole polarizabilities  $\alpha_l$  of order  $l$ . Also,  $\zeta$  is the nonadiabatic correction to  $\eta$ , and  $\theta$  is the nonadiabatic correction to  $\varepsilon$ . The multipole contributions to each term are listed under  $l, l', \dots$

Coeffi-		Coeffi-							
cient	Value	$l$	$l'$	cient	Value	$l$	$l'$	$l''$	$l'''$
$\alpha_1$	$\frac{9}{2Z^4}$	1	1	$\delta_1$	$\frac{9673}{1152Z^{10}}$	1	1		
$\alpha_2$	$\frac{15}{Z^6}$	2	2	$\eta_1$	$\frac{213}{2Z^8}$	1	1	2	
$\alpha_3$	$\frac{525}{4Z^8}$	3	3	$\zeta_1$	$\frac{28\,491}{8Z^{10}}$	1	1	2	
$\alpha_4$	$\frac{8505}{4Z^{10}}$	1	1	$\kappa$	$\frac{1620}{Z^{10}}$	1	2	3	
$\beta_1$	$\frac{43}{8Z^6}$	1	1	$\lambda$	$\frac{9673}{1152Z^{10}}$	2	2	2	
$\beta_2$	$\frac{107}{8Z^6}$	2	2	$\varepsilon$	$\frac{4329}{322Z^{10}}$	1	1	1	1
$\beta_3$	$\frac{3265}{32Z^6}$	3	3	$\theta$	$\frac{534\,323^a}{64Z^{12}}$	1	1	1	1
$\gamma_1$	$\frac{319}{48Z^8}$	1	1	$\rho$	$\frac{4905}{2Z^{12}}$	1	1	1	3
$\gamma_2$	$\frac{2399}{192Z^{10}}$	1	1	$\sigma$	$\frac{98\,511}{16Z^{12}}$	1	2	1	2

<sup>a</sup> Corrected by Xiao-Feng Wang and Zong-Chao Yan, Phys. Rev. A **95**, 022505 (2017).

The complete asymptotic expansion for helium up to  $\langle x^{-10} \rangle$  is

$$\begin{aligned}
E_{nL} = & -2 - \frac{1}{2n^2} + \frac{1}{2} \left\{ -\frac{9}{32} \langle x^{-4} \rangle + \frac{69}{256} \langle x^{-6} \rangle + \frac{3833}{7680} \langle x^{-7} \rangle \right. \\
& - \left[ \frac{55\,923}{32\,768} + \frac{957}{5120} L(L+1) \right] \langle x^{-8} \rangle - \frac{908\,185}{344\,064} \langle x^{-9} \rangle \\
& + \left. \left[ \frac{4\,102\,258}{524\,288} + \frac{33\,275}{14\,336} L(L+1) \right] \langle x^{-10} \rangle \right\} \\
& + e_{2,0}^{1,1} - \frac{23}{20} e_{2,0}^{1,2}
\end{aligned} \tag{21}$$

The last two terms are small second-order dipole-dipole and dipole-quadrupole perturbation corrections. See also Xiao-Feng Wang and Zong-Chao Yan, Phys. Rev. A **95**, 022505 (2017).

For expectation values of  $\langle x^{-n} \rangle$ , see G. W. F. Drake and R. A. Swainson, Phys. Rev. A **42**, 1123 (1990).

For a similar asymptotic expansion of matrix elements of the  $\delta$  function, see G. W. F. Drake, Phys. Rev. A **45**, 70 (1992). This is very useful for QED corrections.

The numerical values of all these terms for the example of the  $1s10$  state are as listed in

### Asymptotic expansion for the energy of the $1s10k$ state of helium

Quantity	Value
$-Z^2/2$	-2.000 000 000 000 000 00
$-1/(2n^2)$	-0.005 000 000 000 000 00
$c_4\langle r^{-4}\rangle$	-0.000 000 007 393 341 95
$c_6\langle r^{-6}\rangle$	0.000 000 000 004 980 47
$c_7\langle r^{-7}\rangle$	0.000 000 000 000 278 95
$c_8\langle r^{-8}\rangle$	-0.000 000 000 000 224 33
$c_9\langle r^{-9}\rangle$	-0.000 000 000 000 002 25
$c_{10}\langle r^{-10}\rangle$	0.000 000 000 000 003 73
Second order	-0.000 000 000 000 070 91
Total	-2.005 000 007 388 376 30(74)
Variational	-2.005 000 007 388 375 8769(0)
Difference	-0.000 000 000 000 000 42(74)
	$\simeq 3 \text{ Hz}$

For a similar application to the Rydberg states of lithium, see R.J. Drachman and A.K. Bhatia, Phys. Rev. A **51**, 2926 (1995).

For the low-lying  $S$ -states and  $P$ -states of helium [?],

$$\ln k_0(1^1S) = 2.983\,865\,861, \quad (22)$$

$$\ln k_0(2^1S) = 2.980\,118\,365, \quad (23)$$

$$\ln k_0(2^3S) = 2.977\,742\,459, \quad (24)$$

$$\ln k_0(2^1P) = 2.983\,803\,377, \quad (25)$$

$$\ln k_0(2^3P) = 2.983\,690\,995. \quad (26)$$

For a  $1snl$  state with large  $l$ , the asymptotic expansion [G.W.F. Drake, Phys. Scr. **T95**, 22 (2001)].

$$\begin{aligned} \ln k_0(1snl) \sim & \ln k_0(1s) + \frac{1}{n^3} \left( \frac{Z-1}{Z} \right)^4 \ln k_0(nl) \\ & + 0.316\,205(6) Z^{-6} \langle r^{-4} \rangle_{nl} \\ & + \Delta\beta(1snl) \end{aligned} \quad (27)$$

becomes essentially exact. Here  $\ln k_0(nl)$  is the one-electron Bethe logarithm  $\ln k_0 = 2.984\,128\,555\,765\,497\,610 \dots$  and

$$\langle r^{-4} \rangle_{nl} = \frac{16(Z-1)^4 [3n^2 - l(l+1)]}{(2l-1)2l(2l+1)(2l+2)(2l+3)}. \quad (28)$$

The correction  $\Delta\beta(1snl)$  for higher order terms is

$$\begin{aligned} \Delta\beta(1snl \ ^1L) = & 95.8(8) \langle r^{-6} \rangle - 845(19) \langle r^{-7} \rangle \\ & + 1406(50) \langle r^{-8} \rangle \end{aligned} \quad (29)$$

$$\begin{aligned} \Delta\beta(1snl \ ^3L) = & 95.1(9) \langle r^{-6} \rangle - 841(23) \langle r^{-7} \rangle \\ & + 1584(60) \langle r^{-8} \rangle. \end{aligned} \quad (30)$$

For example, for the  $1s4f \ ^1F$  state,  $\beta(4 \ ^1F) = 2.984\,127\,1493(3)$ .

# 1 Pseudospectral Theory

The basic idea of pseudospectral methods is to span the actual spectrum of states (i.e. an infinity of bound states plus the continuum) with a basis set of variationally determined pseudostates that is entirely discrete, as illustrated in Fig. 1 (below). In the one-electron case, the discrete variational representation is entirely equivalent to a Sturmian basis set (see Ince" Differential Equations). From a computational point of view, the pseudospectrum is obtained by diagonalizing  $H_0$  in a discrete variational basis set of nonorthogonal functions  $\chi_p$ ,  $p = 0, \dots, N - 1$  such that the linear combinations  $\phi_p = \sum_{q=0}^{N-1} a_{p,q} \chi_q$  satisfy the generalized eigenvalue problem

$$\langle \phi_p | \phi_q \rangle = \delta_{p,q} \tag{31}$$

$$\langle \phi_p | H_0 | \phi_q \rangle = \varepsilon_p \delta_{p,q} \tag{32}$$

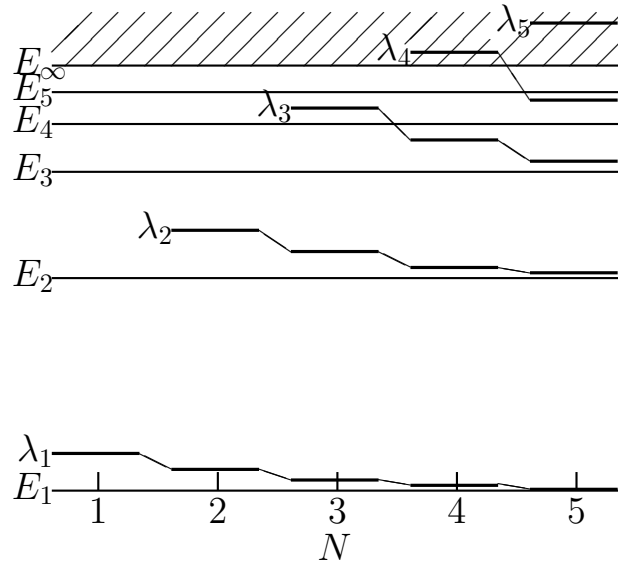


Diagram illustrating the Hylleraas-Undheim-MacDonald Theorem. The  $\lambda_p$ ,  $p = 1, \dots, N$  are the variational eigenvalues for an  $N$ -dimensional basis set, and the  $E_i$  are the exact eigenvalues of  $H$ . The highest  $\lambda_p$  lie in the continuous spectrum of  $H$ .

## Hylleraas-Undheim-MacDonald Theorem

- 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.  
No further orthogonalization is required.

## Demonstration: Pseudostates for Hydrogen Polarizability

Consider as an example the static dipole polarizability  $\alpha_d$  of a hydrogen atom defined by

$$\Delta E = -\frac{1}{2}\alpha_d \mathcal{E}^2$$

where  $\mathcal{E}$  is the external electric field strength. Then

$$\alpha_d = 2 \sum_h' \frac{\langle 1s | z | np \rangle \langle np | z | ns \rangle}{E(2p) - E(1s)}$$

where  $\sum_h'$  denotes a sum over bound states and an integration over the continuum. Alternatively, from perturbation theory,

$$\alpha_d = 2 \langle 1s | z | 1s \rangle^{(1)}$$

where  $|1s\rangle^{(1)}$  denotes the solution to the first-order perturbation equation

$$(H_0 - E_0) |1s\rangle^{(1)} + z |1s\rangle^{(0)} = 0$$

The exact solution to the first-order perturbation equation is

$$\langle \mathbf{r} | 1s \rangle^{(1)} \equiv \Psi^{(1)} = -\frac{1}{\sqrt{3}}(2r + r^2) e^{-r} Y_1^0(\hat{\mathbf{r}}). \quad (33)$$

Construct a variational solution

$$\Psi_{\text{tr}}^{(1)} = -\frac{1}{\sqrt{3}}(b_1 r + b_2 r^2) e^{-\lambda r} Y_1^0(\hat{\mathbf{r}}), \quad (34)$$

where  $b_1$  and  $b_2$  are linear variational parameters, and  $\lambda$  is an additional non-linear variational parameter.

This provides a two-dimensional basis set of functions

$$r e^{-\lambda r} Y_1^0(\hat{\mathbf{r}}) \text{ and } r^2 e^{-\lambda r} Y_1^0(\hat{\mathbf{r}}),$$

with the exact solution being recovered for the case  $\lambda = 1$ .

For  $\lambda \neq 1$ , the basis set provides the best variational representation of  $\Psi^{(1)}$ .

After solving for the pseudostates and summing, the expression for  $\alpha_d$  as a function of  $\lambda$  becomes

$$\alpha_d(\lambda) = 6\lambda^5 \left( \frac{2}{\lambda+1} \right)^{12} \times \frac{9\lambda^4 - 12\lambda^3 + 14\lambda^2 - 10\lambda + 5}{5\lambda^4 - 10\lambda^3 + 18\lambda^2 - 10\lambda + 5}. \quad (35)$$



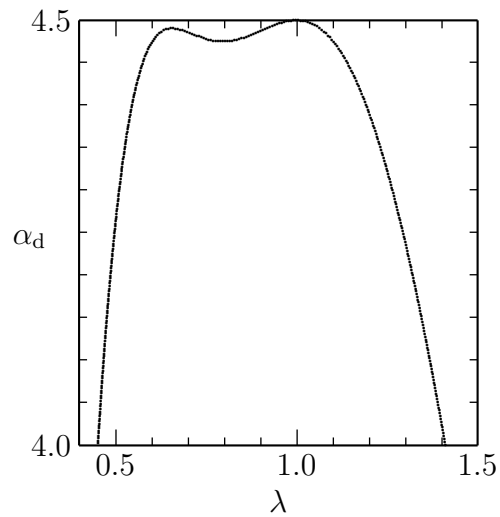


Figure 1: Variational polarizability  $\alpha_d$  of hydrogen.

Main points:

- Since  $E$  is an upper bound,  $\alpha_d$  is a lower bound for any  $\lambda$ .
- The exact value of  $4.5 a_0^3$  is recovered at  $\lambda = 1$  (not  $\lambda = 1/2$  for the 2p state).
- The entire spectrum of hydrogen is being well represented by just two pseudostates, neither of which corresponds to physical states of hydrogen.
- In the sum over the physical spectrum, only about half of the polarizability comes from the bound states. The rest comes from the integration over the continuum.

Hydrogen Polarizability for Different Basis Set Sizes

