Special Topics on Precision Measurement in Atomic Physics: Lecture 6

High Precision Results for Nonrelativistic Energies: Helium

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REVIEW: WAVE FUNCTIONS

Recall that with a doubled basis set, the wave function has the form

$$\Psi = c_0 \Psi_0 + \sum_{ijk}^{i+j+k \le \Omega} \left[\underbrace{c_{ijk}^{(A)} \varphi_{ijk}(\alpha_A, \beta_A)}_{A-\text{sector}} + \underbrace{c_{ijk}^{(B)} \varphi(\alpha_B, \beta_B)}_{B-\text{sector}} \right]$$
(1)

where Ψ_0 is the screened hydrogenic term and the basis functions $\varphi_{ijk}(\alpha, \beta)$ are defined by

$$\varphi_{ijk}(\alpha,\beta) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1,l_2,L}^M(\hat{r}_1,\hat{r}_2) \pm \text{exchange}$$
(2)

The parameter $\Omega = (i + j + k)_{\max}$ controls the size of the basis set. The nominal number of terms in each sector is

$$N = \frac{1}{6}(\Omega + 1)(\Omega + 2)(\Omega + 3)$$
(3)

OPTIMIZATION OF NONLINEAR PARAMETERS

The four α 's and β 's are determined by calculating analytically the the derivatives $\partial E/\partial \alpha_p$ and $\partial E/\partial \beta_p$, p = A, B, and finding the simultaneous zeros by Newton's method. The optimization producers a natural separation of the basis set into two distinct sectors with different distance scales, as illustrated in the following diagram for the 1s2p ¹P state of helium:

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High Precision Theory of Atomic Helium



Fig. 3. Variation of the exponential scale factors with basis set size for the helium 1s2p¹P state.

Key Points:

- α_A and β_A are nearly constant, independent of Ω . These define the long-range asymptotic A-sector of the wave function.
- $\alpha_{\rm B}$ and $\beta_{\rm B}$ increase roughly linearly with Ω . These define the close-range highly correlated B-sector of the wave function.

- It is essential for the linear increase in $\alpha_{\rm B}$ and $\beta_{\rm B}$ to continue in order to avoid computational linear dependence and loss of significant figures in the basis set.
- Note that the function $r^{\Omega} e^{-\alpha r}$ peaks at a constant distance r_{\max} if $\alpha = \Omega/r_{\max}$. Thus the linear increase in $\alpha_{\rm B}$ and $\beta_{\rm B}$ corresponds to a B-sector that peaks at a constant distance r_{\max} from the origin, while the A-sector spreads outward with increasing Ω .
- Doubling of the basis set is only effective for $\Omega \ge 4$. The basis set must be sufficiently large!

Convergence Study for the Ground State of Helium

The following table presents a convergence study for the ground state of helium, and comparison with other calculations.

Key Points:

- Other calculations are more accurate, but at the expense of using multipleprecision arithmetic. For example, the 40-digit calculation of Nakashima and Nakatusji required 120-digit arithmetic and much larger basis sets. Schwartz's calculation required 104-digit arithmetic. Both included logarithmic terms and half-integral powers, thus making integrations more difficult.
- The present results with double basis sets are accurate to 21-digits and required only standard quadruple precision arithmetic (about 32 decimal digits). The program therefore runs orders of magnitude faster and the wave functions are useful for other applications. This level of accuracy is more than sufficient for all practical purposes.

The quantity ${\cal R}$ in the last column gives the ratio of successive differences defined by

$$R = \frac{E(\Omega - 2) - E(\Omega - 1)}{E\Omega - 1 - E\Omega}$$
(4)

Ω	N	$E(\Omega)$	$R(\Omega)$
8	269	-2.903 724 377 029 560 058 400	
9	347	-2.903724377033543320480	
10	443	-2.903724377034047783838	7.90
11	549	-2.903724377034104634696	8.87
12	676	-2.903724377034116928328	4.62
13	814	-2.903724377034119224401	5.35
14	976	-2.903724377034119539797	7.28
15	1150	-2.903724377034119585888	6.84
16	1351	-2.903724377034119596137	4.50
17	1565	-2.903724377034119597856	5.96
18	1809	-2.903724377034119598206	4.90
19	2067	-2.903724377034119598286	4.44
20	2358	-2.903724377034119598305	4.02
Extrapolation [1]	∞	-2.903724377034119598311(1)	
Nakashima [2]	22000	-2.903 724 377 034 119 598 311 15	9 245 194 404 446 696 905 37
Schwartz [3]	10259	-2.903 724 377 034 119 598 311 15	9 245 194 404 440 0
Schwartz extrap.	∞	-2.903 724 377 034 119 598 311 15	9 245 194 404 446
Korobov [4]	5200	-2.903 724 377 034 119 598 311 15	87
Korobov extrap.	∞	-2.903 724 377 034 119 598 311 15	94(4)
Goldman [5]	8066	-2.90372437703411959382	
Bürgers et al. [6]	24 497	-2.903724377034119589(5)	
Baker et al. [7]	476	-2.903 724 377 034 118 4	

Convergence study for the ground state of helium [1].

[1] G.W.F. Drake, M.M. Cassar, and R.A. Nistor, Phys. Rev. A 65, 054501 (2002).

[2] H. Nakashima and H. Nakatsuji, J. Chem. Phys, 127, 22404 (2007)

[3] C. Schwartz, Int. J. Mod. Phys. E 15, 877 (2006)

[4] V.I. Korobov, Phys. Rev. A 66, 024501 (2002).

[5] S.P. Goldman, Phys. Rev. A 57, R677 (1998).

[6] A. Bürgers, D. Wintgen, J.-M. Rost, J. Phys. B 28, 3163 (1995).

[7] J.D. Baker, D.E. Freund, R.N. Hill, J.D. Morgan III, Phys. Rev. A 41, 1247 (1990).

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To the extent that R = constant, the series converges like a geometric series and can be summed to infinity.



$$E(\infty) = \frac{E(\Omega_{\max})}{R-1} \tag{5}$$

Variation of the α s and β 's for a triple basis set for the ground state of helium [Data from G.W.F. Drake, M.M. Cassar, and R.A. Nistor, Phys. Rev. A **65**, 054501 (2002).]

160 / Atomic, Molecular, and Optical Physics Handbook

Table 11.2. Nonrelativistic eigenvalue coefficients c_0 and c_1 for helium.

Table	11.3.	Eigenvalue	coefficients	c2 for	helium.
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$ \begin{array}{c} s_{1}(n^{2}L) & (r_{1}(n^{2}L) &$							and	the second of the second second
$ \begin{array}{c} 1.5 & -2.80 \ 72.4177 \ (0.614196) \ (0.009 \ 81384 \ 41298 \ -2.1175 \ 229 \ 578 \ 225 \ 711 \ 30 \ 0.007 \ 421 \ 1007 \ 600 \ 412 \ 1007 \ 615 \ 412 \ 500 \ 410 \ 410 \ 500 \ 810 \ 410 \ 510 \ 410 \ 510 \ 410 \ 5$	State	$\varepsilon_0(n L)$	$\varepsilon_1(n^4L)$	$\varepsilon_0(n^3L)$	$\varepsilon_1(n^{-3}L)$	State	$\mathcal{L}_2(n^{-1}L)$	$\varepsilon_2(n^3L)$
$ \begin{array}{c} 2s-2.148 97406 664 10(6) \\ p-2.153 6450 64966 920 \\ p-2.163 8406 64966 920 \\ p-2.064 100 640 6426 940 71) \\ p-2.064 114 920 710 710 710 710 710 710 710 71$	15-	-2.903 724 377 034 119 5	0.159 069 475 085 84			15	-0.470391870(1)	And the second second
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2 S -	-2.145 974 046 054 419(6)	0.009 503 864 419 28	-2.175 229 378 236 791 30	0.007 442 130 706 04	25	-0.135 276 864(1)	-0.057 495 847 9(2)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	2 P -	-2.123843086498093(2)	0.046 044 524 937(1)	-2.133164190779273(5) -	-0.064 572 425 024(4)	2P	-0.168 271 22(7)	-0.20495988(1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	35-	-2.061271989740911(5)	0.002 630 567 097 7(1)-	-2.06868906747245719	0.001 896 211 617 81	35	-0.058 599 3124(4)	-0.040 455 850 5(5)
$ \begin{array}{c} 3 \ D = 0.055 \ 2013 \$	3 P -	-2.05514636209194(3)	0.014 548 047 097(1)	-2.05808108427428(4)	-0.018369001636(2)	3 P	-0.066 047 859(3)	-0.070292710(2)
$ \begin{array}{c} 4S - 2033 86717 (3072) (1) & 0.001 073641226 (1) - 2.0023 424 54266 (2) & -0.007555 1786 (1) & 4P & -0.003 15971 (6) & -0.005 15973 (2) \\ 4D - 2.031 07964 0786 (377) & -0.000 129175 1887 (8) - 2.031 288 447 501 796 (3) & -0.0000 9596 426 56 (2) & 4P & -0.031 274 593 (6) & -0.001 274 593 (7) \\ 5S - 2.021 176551 574 353 (5) & 0.000 3586 0305 (1) - 2.022 615 872 302 312 271 (1) & -0.0035 1697 1165 49 & 5S & -0.003 1574 56 (6) & -0.011 272 9790 1 (3) \\ 5S - 2.021 176551 574 353 (5) & 0.000 3586 0305 (1) - 2.022 615 872 302 312 271 (1) & -0.0035 1091 105 (1) & 5S & -0.003 154 176 (3) & -0.001 272 496 (1) \\ 5D - 2.009 015581 1594 9(4) & -0.0000 577 1492 (7) & -2.0000 107 456 (115) & -0.0000 1046 001 3 & 5S & -0.0020 1510 (2) & -0.019 756 (2) \\ 5C - 2.021 176551 1574 237 (3) & -0.0000 577 143 (2) -2.0000 273 573 736 (4) & -0.00000 56 65 (6) & -0.020 013 56 (6) & -0.020 013 56 (6) \\ 5C - 2.012 450 944 66 (1) & -0.0000 297 744 577 10 & -0.0000 140 601 3 & 5C & -0.020 013 56 (6) & -0.020 013 56 (6) \\ 6C - 2.013 580 547 (5) & -0.000 045 74 122 587 (7) - 2.011 379 928 57 137 (1) & -0.0000 140 601 3 & 5C & -0.012 401 796 (4) & -0.012 411 399 (1) \\ 6C - 2.013 580 545 (5) & -0.000 048 51 22 57 (7) - 2.011 387 068 74 37 (1) & -0.0000 124 51 26 (8) & 6F & -0.011 489 14 (2) & -0.013 581 (2) \\ 6C - 2.013 580 542 (7) & -0.000 048 51 72 (7) & -2.011 389 068 54 52 29 (2) & -0.0000 088 (52 17 (7) & 6G & -0.011 389 (5) (4) & -0.011 389 (2) (2) \\ 7S - 2.010 61 51 52 03 (7) & -0.000 048 51 72 (7) & -2.011 289 068 51 (2) & -0.0000 000 85 (22 17 (7) & -0.011 289 (2) (2) & -0.011 289 (2) (2) \\ 7F - 2.010 163 51 56 (7) & -0.000 049 51 17 + 2.013 580 068 (4) 22 (7) & -0.0000 000 58 (52 17 (7) & -0.011 289 (2) (2) & -0.011 289 (2) (2) \\ 7F - 2.010 163 51 56 (7) & -0.000 02 92 57 (1) + 2.011 129 015 (15 56 31 (1) & -0.0000 02 156 (1) & 7F & -0.010 286 (5) (7) & -0.011 289 (2) (2) \\ 7F - 2.010 163 51 56 (7) & -0.000 02 000 (11 75 55 57 (1) & -0.000 02 56 (56 (3) (7) & -0.0000 02 56 (56 (3) (7) & -0.0000 02 56 (56 (3) (7) & -0.0000 02 56$	3 D -	-2.055 620 732 852 246(6)	-0.000 249 399 992 1(1)	-2.055636309453261(4)	0.000025322839(1)	3 D	-0.057 201 299(9)	-0.05473773(1)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	48-	-2.033 586 717 030 72(1)	0.001 073 641 226 6(1)	-2.03651208309823630(2)	0.00074266151618	45	-0.032522293(2)	-0.025 628 633 8(1)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	4 P -	-2.031 069 650 450 24(3)	0.006 254 923 554 3(1)	-2.03232435429662(2)	-0.00755517898(1)	4P	-0.035 159 71(6)	-0.036129973(2)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	4 D -	-2.031 279 846 178 687(7)	-0.0001291751887(8)-	-2.031288847501795(3)	0.000029442651(2)	A D	-0.03215091(2)	-0.030747891(7)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	4 F -	-2.031 255 144 381 749(1)	-0.000 010 024 269 4(2)-	-2.031 255 168 403 245 6(6) -	-0.000 009 669 639 6	4F	-0.031274336(4)	-0.031 277 992 1(3)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	55-	-2.021 176 851 574 363(5)	0.000 538 860 360 5(1)	-2.02261887230231227(1)	0.000 363 697 136 49	5.5	-0.02064726(9)	-0.017 999 794 96
$ \begin{array}{c} 5 D - 2020015836159964(4) & -0.00007188131(6) & -2.02002102744591(5) & 0.00001965888(1) & 5 D & -0.02013498(6) & -0.020101561(4) \\ 5 F - 2.02003971587267(7) & -0.000007192946(4) & -2.020009716729234392(1) & -0.000019404013 & 5 F & -0.02013498(6) & -0.020101561(4) \\ 5 G - 2.01338539767173(2) & 0.0017870427(1) & -2.01537742292928219(3) & 0.0020432947910 & 6 S & -0.012861996(4) & -0.0124113991(3) \\ 6 F - 2.01338539767173(2) & 0.00178704527(3) & -2.0153774(1) & -0.000114344643(1) & 6 F & -0.011499(2) & -0.01370727(1) \\ 6 F - 2.013389527424296(5) & -0.000048412258(7) & -2.015389046344352(2) & -0.0000003264458(6) & 6 - 0.01189698(3) & -0.01339922(3) \\ 6 G - 2.013895341542973(2) & -0.0000003952727(7) & -2.0138980457430150 & -0.0000003934457 & 6 G & -0.01389619(1) & -0.013891148(8) \\ 6 H - 2.01389341542935(2) & -0.000000290371 & -2.0138901451635800457430150 & -0.0000002934457 & 6 G & -0.013896191 & -0.0138986190 \\ 7 F - 2.0101639142923(2) & -0.00000290371 & -2.01389014753015 & -0.0000002934457 & 6 G & -0.011489(2) & -0.00163896191 \\ 7 F - 2.0101241429245(2) & -0.000149600797(2) & -0.001656308(3) & 7 F & -0.010485(2) & -0.0016379(2) \\ 7 D - 2.001163142935(2) & -0.000002907540(2) & -2.010212105855505(2) & -0.0000000565121(3) & 7 D & -0.00164850(3) & -0.0104852(2) \\ 7 F - 2.0102924874748(2) & -0.0000002910755 & 711441206619132 & -0.00020923457 & -0.001204507(3) & -0.01023457(5) \\ 7 F - 2.0102924874745(2) & -0.000002917755 & -2.0102412205857485(2) & -0.000000777755 & 71 & -0.010242477 & -0.01023457(5) \\ 7 F - 2.0102924579250(7) - 0.0000002989953(3) - 2.0102412805651292(1) & -0.00000029107755 & 71 & -0.0102942(3) & -0.001028587485(5) & -0.00777755 & -0.0012942577 & -0.0002942775 & -0.00778158(2) \\ 8 F - 2.00778127114940619132 & -0.00000291976181(1) - 2.007812785165365(1) & -0.000000377755 & 71 & -0.0102342767 & -0.0002342775 & -0.0077815285(2) & -0.0077815285(2) & -0.0077815285(2) & -0.0077815285(2) & -0.0077815285(2) & -0.0077815285(2) & -0.0077815285(2) & -0.0077815285(2) & -0.00077815285(2) & -0.0000003977755 & 7$	5 P -	-2.019 905 989 900 83(2)	0.003 230 021 84(2)	-2.020 551 187 256 25(1)	-0.003810911035(1)	5 P	0.021 8476(9)	0.022 166 61 (0)
$ \begin{array}{c} 5P - 0.020 \ 0.0987 \ 1587 \ 427 \ 620 \ 0.000 \ 0.000 \ 100 \ 420 \ 640 \ 640 \ 650 \ 550 \ -0.020 \ 0.0000 \ 650 \ 640 \ 640 \ 650 \ 550 \ -0.020 \ 0.0000 \ 650 \ 650 \ 650 \ -0.020 \ 0.0000 \ 650 \ 650 \ 650 \ -0.020 \ 0.0000 \ 650 \ 650 \ 650 \ -0.020 \ 0.0000 \ 650 \ 650 \ -0.020 \ 0.0000 \ 650 \ 650 \ -0.020 \ 0.0000 \ 650 \ 650 \ -0.020 \ 0.0000 \ 650 \ 650 \ -0.0000 \ 650 \ -0.0000 \ 650 \ -0.0000 \ -0.0000 \ -0.000 \ -0.000 \ -0.000 \ -0.0000 \ -0.000$	5 D -	-2 020 015 836 159 984(4)	-0.000071883131(6)	-2.020021027446911(5)	0.00001956885(1)	5 0	-0.0218470(3)	-0.02210001(9)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	5 F -	-2 020 002 937 158 742 7(5)	-0.000 005 704 294 6(4)-	-2.0200029573773694(4)	-0.000.005 406 490 0(5)	5 L)	0.020 010 1(2)	0.000.010 2(2)
$ \begin{array}{c} 6S & -2.014 \ \text{s} 83984 \ \text{s} 44660(1), \\ 0.000 \ 317 \ 704 \ 277(1) & -2.015 \ 377 \ 425 \ 929 \ 825 \ 19(3) \ 0.000 \ 204 \ 829 \ 479 \ 10 \\ 6S & -0.014 \ 435 \ 308 \ -0.0012 \ 411 \ 391 \ (3) \\ 6F & -2.013 \ 839 \ 757 \ 7(2) \ 0.000 \ 876 \ 853 \ 856(1) \ -2.014 \ 437 \ 958 \ 737 \ 7(1) \ -0.002 \ 143 \ 346 \ 451(1) \\ 6F & -2.013 \ 839 \ 455 \ 100 \ 876 \ 875 \ 877 \ 7(2) \ 0.000 \ 876 \ 853 \ 856(1) \ -2.014 \ 437 \ 958 \ 737 \ 7(1) \ -0.002 \ 143 \ 346 \ 451(1) \\ 6F & -2.013 \ 890 \ 653 \ 152 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 100 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 100 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 100 \ 977 \ -2.013 \ 890 \ 454 \ 357 \ 100 \ 977 \ -2.013 \ 890 \ 441 \ 353 \ 577 \ -2.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 127 \ 77 \ -0.010 \ 890 \ 554 \ 17 \ 77 \ -0.010 \ 890 \ 554 \ 17 \ 77 \ -0.010 \ 890 \ 554 \ 17 \ 77 \ -0.010 \ 890 \ 554 \ 17 \ 77 \ -0.010 \ 890 \ 554 \ 17 \ 77 \ -0.010 \ 890 \ 554 \ 17 \ 77 \ -0.010 \ 890 \ 557 \ 17 \ -0.010 \ 890 \ 557 \ 17 \ -0.010 \ 890 \ 557 \ 17 \ -0.010 \ 890 \ 557 \ 17 \ -0.010 \ 890 \ 57 \ 17 \ -0.010 \ 890 \ 57 \ 17 \ -0.010 \ 890 \ 57 \ 17 \ -0.010 \ 890 \ 57 \ 17 \ -0.010 \ 890 \ 57 \ 17 \ -0.010 \ 890 \ 57 \ 17 \ -0.010 \ 890 \ 57 \ 17 \ -0.010 \ 890 \ 57 \ 17 \ -0.010 \ 890 \ 57 \ 17 \ -0.0007 \ 817 \$	50-	2 020 000 710 898 584 71(1)	0 000 001 404 4136	2 020 000 710 925 343 92(1)	0 000 001 404 001 3	21	-0.020 013 498(6)	-0.020 010 361(4)
$ \begin{array}{c} 6P - 2.013833979 67173(2) \\ 6P - 2.0138333979 67173(2) \\ 0.001878 0083 036(1) \\ - 2.0138995277 42486(5) \\ - 0.0010000 12412269(6) \\ - 0.0113890 53355(5) \\ - 0.0011221208658 01529(7) \\ - 0.0010000 0000 2085 5799(7) \\ - 2.013890 5345527 (2120) \\ - 0.0113890 5345527 (2120) \\ - 0.0113890 22(3) \\ - 0.001000 0000 2085 5799(7) \\ - 2.013890 3454 55320(2) \\ - 0.000000 20234576 \\ - 2.013890 3454 55313 22(3) \\ - 0.0000 000 900 3451 520(1) \\ - 2.0113890 3454 5015 \\ - 0.000000 2023457 \\ - 0.0118850 1179(6) \\ - 0.011880 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.0108 5109 \\ - 0.010 200 \\ - 0.0108 5100 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.010 200 \\ - 0.000 200 \\ - 0.000 200 \\ - 0.000 200 \\ - 0.000 200 \\ - 0.000 \\ - 0.000 200 \\ - 0.000 200 \\ - 0.000 200 \\ - 0.000 200 \\ - 0.000 200 \\ - 0.000 \\ - 0.000 200 \\ - 0.000 200 \\ - 0.000 200 \\ - 0.000 \\ - 0.000 200 \\ - 0.000 \\ - 0.000 200 \\ - 0.000 \\ - 0.000 200 \\ - 0.000 \\ - 0.000 \\ - 0.000 \\ - 0.000 200 \\ - 0.000$	6.5 -	-2.014 563 008 446 60(1)	0.000 307 704 277(1)	-2 015 377 452 902 862 19(3)	0 000 204 329 479 10	26	-0.020 003 300 8	-0.020 003 564 6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6 P	3 019 899 070 671 79/9)	0.001 878 058 596(1)	2 014 207 058 779 74(1)	0.000184946469(1)	0.0	-0.014 261 796(4)	-0.0124113991(3)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	6 D	9 019 000 997 494 906/5)	0.001 878058 530(1)	2.014.207 998 713 74(1) 9.019.001 415 459 709(7)	0.00001974999(9)	6 P	-0.014 902 86(9)	-0.01503358(5)
$ \begin{array}{c} pr & -2.013 \pm 9869343 \pm 9361 + (3) & -0.000 + 988 \pm 799 + (7) & -0.013 \pm 989 \pm 443 \pm 932 + (2) & -0.000 + 988 \pm 799 + (7) & 6 & -0.013 \pm 986984 + (2) & -0.013 \pm 991 \pm 84 + (8) & -0.013 \pm 989 \pm 184 + (8) & -0.013 \pm 989 \pm 184 + (8) & -0.013 \pm 989 \pm 184 + (8) & -0.011 \pm 991 \pm 925 + (2) & -0.011 \pm 991 \pm 921 \pm 925 + (2) & -0.011 \pm 991 \pm 921 \pm 925 + (2) & -0.011 \pm 991 \pm 925 + (2) & -0.011 \pm 991 \pm 925 + (2) & -0.011 \pm 91 \pm 91 \pm 925 + (2) & -0.011 \pm 91 \pm$	CP	9 019 000 C09 015 540 7(0)	0.000.000.400.000.9(9)	0.010.000.000.0400.192(7)	0.00001214222(3)	6 D	-0.0141994(2)	-0.01370727(1)
$ \begin{array}{c} 6 \ G = -2.013 \ 889 \ 345 \ 337 \ 313 \ 22(3) = -0.000 \ 000 \ 993 \ 417 \ -2.013 \ 889 \ 345 \ 416 \ 652 \ 98(3) \ -0.0000 \ 989 \ 812 \ 37(1) \ 6 \ C \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.013 \ 886 \ 117 \ 9(6) \ -0.010 \ 882 \ 12(3) \ 7 \ P \ -0.010 \ 816 \ 82(2) \ -0.010 \ 818 \ 22(2) \ -0.000 \ 918 \ 12(3) \ 7 \ P \ -0.010 \ 816 \ 82(2) \ -0.010 \ 818 \ 22(2) \ -0.010 \ 818 \ 22(2) \ -0.010 \ 816 \ 82(3) \ 7 \ P \ -0.010 \ 816 \ 82(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.010 \ 816 \ 81(2) \ -0.000 \ 81(2) \ 816 \ 81(2) \ -0.000 \ 81(2) \ 816 \ 81(2) \ -0.000 \ 81(2) \ 816 \ 81(2) \ -0.000 \ 81(2) \ 816 \ 81(2) \ -0.000 \ 81(2) \ 816 \ 81(2) \ -0.000 \ 81(2) \ 817 \ 816 \ 817 \ 817 \ 816 \ 817 \ $	OF-	-2.013 890 683 815 549 7(3)	-0.000003482257(7)	-2.013 890 698 348 5320(2)	0.0000032684586(8)	6 F	-0.013896984(2)	-0.01389922(3)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	66-	-2.013 889 345 387 313 22(3)	-0.000 000 898 579 9(7)-	-2.013 889 345 416 952 96(3)-	-0.0000008981237(7)	6 G	-0.013 891 179(6)	-0.013891184(8)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	6 11 -	-2.013 889034 754 279 72	-0.000 000 290 347 1	-2.013 889 034 754 301 55	-0.000 000 290 346 7	6 H	-0.0138896191	-0.013 889 619 0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	75-	-2.01062577621087(2)	0.000 191 925 025(1)	-2.01112991952762621(4)	0.00012598173689	75	-0.0104382(2)	-0.0093044433(3)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	7 P -	-2.01016931452935(2)	0.001 186 152 30(1)	-2.01040496000794(2) -	-0.0013665008(3)	7P	-0.0108186(2)	-0.010879(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	7 D -	-2.01021002845798(1)	-0.000028027840(2)	-2.010212105955595(2)	0.000008563121(3)	7 D	-0.010 405 09(3)	-0.010085212(1)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	7F -	-2.010205248074013(1)	-0.00000226200(4)	-2.010205258374865(1)	-0.00000211058(3)	7F	-0.0102092(3)	-0.010 210 7(3)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	7G -	-2.01020438622477255(7)	-0.0000005983963(3)	-2.010 204 386 250 217 93(6)	-0.000000598005(1)	7 G	-0.010 205 61(5)	-0.010 205 61(5)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	7 H -	-2.01020418280648204(2)	-0.000 000 201 097 8	-2.01020418280651204(1)	-0.0000002010973	7H	-0.010204590(2)	-0.010204587(2)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	71 -	-2.010 204 120 606 191 32	-0.000 000 077 775 5	-2.010 204 120 606 191 340	-0.0000000777755	71	-0.010 204 276 7	-0.010 204 276 8
$\begin{array}{llllllllllllllllllllllllllllllllllll$	85 -	-2.00809362210561(4)	0.000127650436(1)	-2.00842712206472142(6)	0.000 083 070 552 34	85	-0.007968944(3)	-0.007 224 770 5(3)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	8 P -	-2.00778912713322(2)	0.00079619583(5)	-2.00794701377112(1)	-0.0009110535(3)	8 P	-0.008 211 7(5)	-0.008 2487(6)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	8 D -	-2.007 816 512 563 811(7)	-0.000019076181(1) -	-2.007817934711706(3)	0.0000059711234(3)	8 D	-0.0079507(4)	-0.00773159(2)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	8F -	-2.007 813 297 115 014 1(6)	-0.000 001 545 48(1)	-2.0078133045350908(5) -	-0.000001 436 452(2)	8 F	-0.0078159(3)	-0.0078170(2)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	8G -	-2.007 812 711 494 024 1(1)	-0.000 000 415 004 0(1)-	-2.007 812 711 514 424 82(9)-	-0.000 000 414 690 4	80	-0.007813563(1)	-0.007.813568(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	8 H -	-2.007 812 571 828 655 81(1)	-0.000 000 142 649 2(3)-	-2.007 812 571 828 685 73(1)-	-0.0000001426487(2)	8 H	-0.007812855(4)	-0.007812859(5)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	81 -	-2.007 812 528 549 584 59	-0.000 000 056 935 9	-2.007 812 528 549 584 61	-0.000 000 056 935 9	81	-0.007 8126420	-0.007 812642.0
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	8 K -	-2 007 812 512 570 229 31	-0.000.000.025.111.3	-2.007 812 512 570 229 306	0 000 000 025 111 3	RK	-0.0078125630	-0.007 812 563.0
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	95-	2 006 369 553 107 85(3)	0.0000891496387(7)	-2.006.601.516.715.010.67(3)	0.00005762831152	0.5	0.006 989 5196/1)	0.005 768 098 5(1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	QP-	2 006 156 384 652 86(5)	0.000 559 978 098(9)	-2.006 267 267 366 41(4)	0 000 637 531 359(6)	0 P	-0.006 282 5130(1)	0.000/08/096 0(1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9.0-	-2 006 175 671 437 641(6)	-0.000.013542185(3)	-2 006 176 684 884 697(2)	0.000.004.306.538(6)	0.0	0.000 970 00(7)	0.000 115 9/1)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Q.F.	-9.0061794068979946(8)	-0.000.001.000.067.1(9).	-2 006 173 419 365 049 0(7)	0 000 001 019651(2)	91	-0.00021099(1)	-0.0001152(1)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	0.0	9.0001134006915240(8)	0.000.000.909.907.1(3)	2.0001134123030430(1)	0.000001019001(2)	91	-0.00617520(1)	-0.0061760254(7)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	0.0	2.0001/299102/3803(2)	0.000.000.104.009.9	2.0061129910430650(3)	0.0000001040010	96	-0.0001733796(1)	-0.006173592(4)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	911-	2.00017289190301914(2)	0.0000001040022	-2.00011289190304588(2)-	0.0000001040019	9 H	-0.006173104(2)	-0.006173101(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	91 -	2.00617286073238257	-0.0000000423136	-2.00617286073238260	-0.0000000423136(1)	91	-0.0061729459(1)	-0.0051729460(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	94-	-2.00617284909632978	-0.0000000191516	-2.006172849096329780 -	-0.000000191516	9 K	-0.0061728876	-0.0061728876
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	105-	-2.00514299174800(8)	0.000 064 697 214(3)	-2.0053107949156113(2)	0.00004159881152	10 5	-0.0050798362(8)	-0.0047094530(1)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10 P -	-2.00498798380222(4)	0.000 408 649 426 3	-2.0050688054978(1)	-0.000463433718(8)	10 P	-0.005197(1)	-0.0052067(1)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	10 D -	-2.005002071654250(6)	-0.000 009 947 506 0(6)	-2.005002818080232(8)	0.000003198298(8)	10 D	-0.0050724(4)	-0.0049580(8)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	10 F -	-2.0050004175646682(9)	-0.000 000 809 442(9)	-2.005 000 421 686 603 6(7)	-0.0000007489264(2)	10 F	-0.00500176(2)	-0.005002386(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10 G -	-2.0050001127643180(3)	-0.000000220982(2) -	-2.0050001127770031(4) -	-0.000000220785(3)	10 G	-0.00500055(2)	-0.00500055(2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10 H -	-2.00500003921439452(2)	-0.000 000 077 806 7	-2.00500003921441741(2)	-0.000 000 077 806 2	10 H	-0.0050001935(2)	-0.0050001935(1)
$10\ K\ -2.005\ 000\ 007\ 388\ 375\ 88\ -0.000\ 000\ 014\ 751\ 4\ -0.005\ 000\ 036\ 9\ -0.005\ 000\ 036\ 000\ 036\ 000\ 036\ 000\ 036\ 000\ 036\ 000\ 036\ 00\ 000\ 0$	10 I -	-2.005 000 016 086 516 19	-0.0000000320590(1)	-2.00500001608651622	-0.0000000320589(2)	10 I	-0.005 000 080 3(4)	-0.005000081(1)
	10 K -	-2.005 000 007 388 375 88	-0.000 000 014 751 4	-2.005 000 007 388 375 88	-0.000 000 014 751 4	10 K	-0.005 000 036 9	-0.005 000 036 8

Note that for high angular momentum, the eigenvalues rapidly approach the screened hydrogenic eigenvalues

$$E_{\rm SH} = -\frac{Z^2}{2} - \frac{(Z-1)^2}{2n^2} \text{ a.u.}$$
(6)

with increasing L, as shown in the following table for L up to 7 (K-states)

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

State	Singlet	Triplet
10 S	-2.005142991747919(79)	-2.0053107949156113(11)
10 P	-2.0049879838022179(26)	-2.0050688054977067(30)
10 D	-2.00500207165425681(75)	-2.00500281808022884(53)
$10 \mathrm{F}$	-2.00500041756466880(11)	-2.00500042168660488(26)
$10 \mathrm{~G}$	-2.005000112764318746(22)	-2.005000112777003317(21)
$10 \mathrm{~H}$	-2.005000039214394532(17)	-2.005000039214417416(17)
10 I	-2.0050000160865161947(3)	-2.0050000160865162194(3)
$10 \mathrm{K}$	-2.0050000073883758769(0)	-2.0050000073883758769(0)

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



Figure showing the physical basis for a core-polarization model in which a Rydberg electron moves in the field generated by a polarizable core.