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

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

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

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

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

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

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 $\partial E/\partial\beta_p$, $p = \mathrm{A}, \mathrm{B}$, 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

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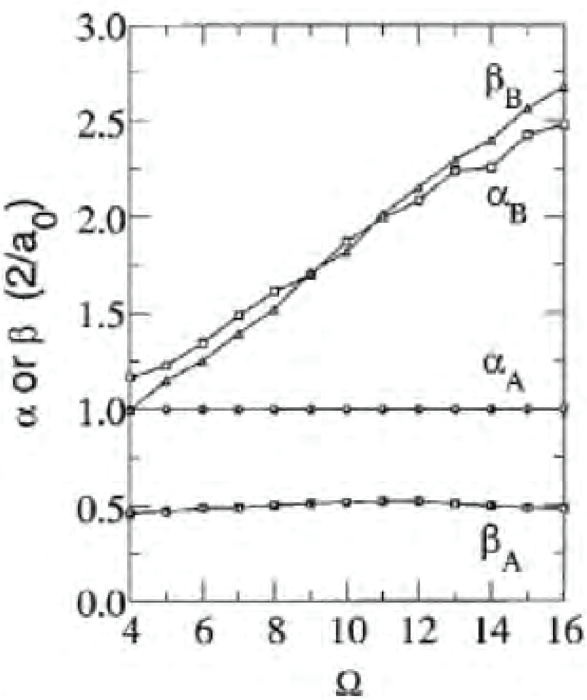


Fig. 3. Variation of the exponential scale factors with basis set size for the helium 1s2p ¹P state.

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.
- α_B and β_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 $r_{\rm max}$ if $\alpha = \Omega/r_{\rm max}$. Thus the linear increase in $\alpha_{\rm B}$ and $\beta_{\rm B}$ corresponds to a B-sector that peaks at a constant distance $r_{\rm max}$ from the origin, while the A-sector spreads outward with increasing Ω.
- Doubling of the basis set is only effective for $\Omega \geq 4$. The basis srt 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 multiple-precision 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 R in the last column gives the ratio of successive differences defined by

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

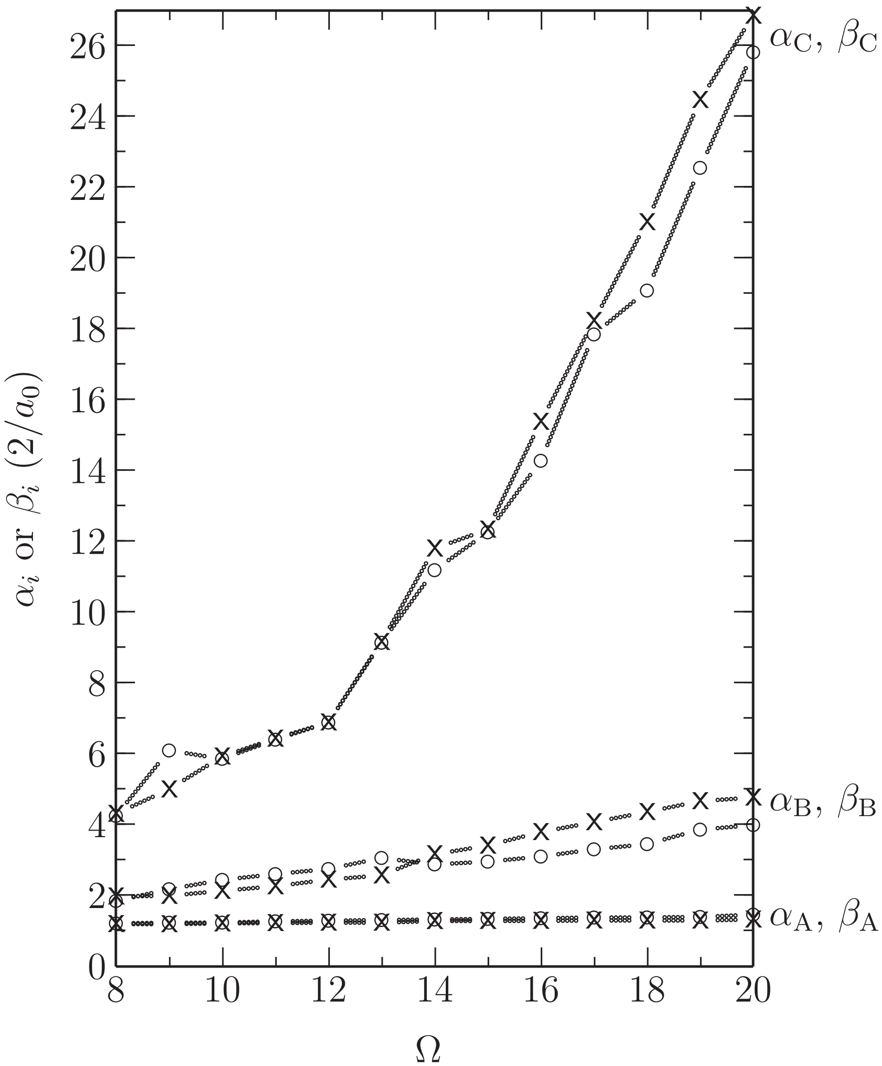
Convergence study for the ground state of helium [1].

Ω	N	$E(\Omega)$	$R(\Omega)$
8	269	–2.903 724 377 029 560 058 400	
9	347	–2.903 724 377 033 543 320 480	
10	443	–2.903 724 377 034 047 783 838	7.90
11	549	–2.903 724 377 034 104 634 696	8.87
12	676	–2.903 724 377 034 116 928 328	4.62
13	814	–2.903 724 377 034 119 224 401	5.35
14	976	–2.903 724 377 034 119 539 797	7.28
15	1150	–2.903 724 377 034 119 585 888	6.84
16	1351	–2.903 724 377 034 119 596 137	4.50
17	1565	–2.903 724 377 034 119 597 856	5.96
18	1809	–2.903 724 377 034 119 598 206	4.90
19	2067	–2.903 724 377 034 119 598 286	4.44
20	2358	–2.903 724 377 034 119 598 305	4.02
Extrapolation [1]	∞	–2.903 724 377 034 119 598 311(1)	
Nakashima [2]	22000	-2.903 724 377 034 119 598 311 159 245 194 404 446 696 905 37	
Schwartz [3]	10259	–2.903 724 377 034 119 598 311 159 245 194 404 440 0	
Schwartz extrap.	∞	–2.903 724 377 034 119 598 311 159 245 194 404 446	
Korobov [4]	5200	–2.903 724 377 034 119 598 311 158 7	
Korobov extrap.	∞	–2.903 724 377 034 119 598 311 159 4(4)	
Goldman [5]	8066	–2.903 724 377 034 119 593 82	
Bürgers *et al.* [6]	24 497	–2.903 724 377 034 119 589(5)	
Baker *et al.* [7]	476	–2.903 724 377 034 118 4	

[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).

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 αs 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).]

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Table 11.2. Nonrelativistic eigenvalue coefficients ε_0 and ε_1 for helium.

State	$\varepsilon_0(n\,^1L)$	$\varepsilon_1(n\,^1L)$	$\varepsilon_0(n\,^3L)$	$\varepsilon_1(n\,^3L)$
1 S	−2.903 724 377 034 119 5	0.159 069 475 085 84		
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
2 P	−2.123 843 086 498 093(2)	0.046 044 524 937(1)	−2.133 164 190 779 273(5)	−0.064 572 425 024(4)
3 S	−2.061 271 989 740 911(5)	0.002 630 567 097 7(1)	−2.068 689 067 472 457 19	0.001 896 211 617 81
3 P	−2.055 146 362 091 94(3)	0.014 548 047 097(1)	−2.058 081 084 274 28(4)	−0.018 369 001 636(2)
3 D	−2.055 620 732 852 246(6)	−0.000 249 399 992 1(1)	−2.055 636 309 453 261(4)	0.000 025 322 839(1)
4 S	−2.033 586 717 030 72(1)	0.001 073 641 226 6(1)	−2.036 512 083 098 236 30(2)	0.000 742 661 516 18
4 P	−2.031 069 650 450 24(3)	0.006 254 923 554 3(1)	−2.032 324 354 296 62(2)	−0.007 555 178 98(1)
4 D	−2.031 279 846 178 687(7)	−0.000 129 175 188 7(8)	−2.031 288 847 501 795(3)	0.000 029 442 651(2)
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
5 S	−2.021 176 851 574 363(5)	0.000 538 860 360 5(1)	−2.022 618 872 302 312 27(1)	0.000 363 697 136 49
5 P	−2.019 905 989 900 83(2)	0.003 230 021 84(2)	−2.020 551 187 256 25(1)	−0.003 810 911 035(1)
5 D	−2.020 015 836 159 984(4)	−0.000 071 883 131(6)	−2.020 021 027 446 911(5)	0.000 019 568 85(1)
5 F	−2.020 002 937 158 742 7(5)	−0.000 005 704 294 6(4)	−2.020 002 957 377 369 4(4)	−0.000 005 406 490 0(5)
5 G	−2.020 000 710 898 584 71(1)	−0.000 001 404 413 6	−2.020 000 710 925 343 92(1)	−0.000 001 404 001 3
6 S	−2.014 563 098 446 60(1)	0.000 307 704 277(1)	−2.015 377 452 992 862 19(3)	0.000 204 329 479 10
6 P	−2.013 833 979 671 73(2)	0.001 878 058 536(1)	−2.014 207 958 773 74(1)	−0.002 184 346 463(1)
6 D	−2.013 898 227 424 286(5)	−0.000 043 412 268 9(9)	−2.013 901 415 453 792(7)	0.000 012 742 22(3)
6 F	−2.013 890 683 815 549 7(3)	−0.000 003 482 257(7)	−2.013 890 698 348 532 0(2)	−0.000 003 268 458 6(8)
6 G	−2.013 889 345 387 313 22(3)	−0.000 000 898 579 9(7)	−2.013 889 345 416 952 96(3)	−0.000 000 898 123 7(7)
6 H	−2.013 889 034 754 279 72	−0.000 000 290 347 1	−2.013 889 034 754 301 55	−0.000 000 290 346 7
7 S	−2.010 625 776 210 87(2)	0.000 191 925 025(1)	−2.011 129 919 527 626 21(4)	0.000 125 981 736 89
7 P	−2.010 169 314 529 35(2)	0.001 186 152 30(1)	−2.010 404 960 007 94(2)	−0.001 366 500 8(3)
7 D	−2.010 210 028 457 98(1)	−0.000 028 027 840(2)	−2.010 212 105 955 595(2)	0.000 008 563 121(3)
7 F	−2.010 205 248 074 013(1)	−0.000 002 262 00(4)	−2.010 205 258 374 865(1)	−0.000 002 110 58(3)
7 G	−2.010 204 386 224 772 55(7)	−0.000 000 598 396 3(3)	−2.010 204 386 250 217 93(6)	−0.000 000 598 005(1)
7 H	−2.010 204 182 806 482 04(2)	−0.000 000 201 097 8	−2.010 204 182 806 512 04(1)	−0.000 000 201 097 3
7 I	−2.010 204 120 606 191 32	−0.000 000 077 775 5	−2.010 204 120 606 191 340	−0.000 000 077 775 5
8 S	−2.008 093 622 105 61(4)	0.000 127 650 436(1)	−2.008 427 122 064 721 42(6)	0.000 083 070 552 34
8 P	−2.007 789 127 133 22(2)	0.000 796 195 83(5)	−2.007 947 013 771 12(1)	−0.000 911 053 5(3)
8 D	−2.007 816 512 563 811(7)	−0.000 019 076 181(1)	−2.007 817 934 711 706(3)	0.000 005 971 123 4(3)
8 F	−2.007 813 297 115 014 1(6)	−0.000 001 545 48(1)	−2.007 813 304 535 090 8(5)	−0.000 001 436 452(2)
8 G	−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
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)	−0.000 000 142 648 7(2)
8 I	−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
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
9 S	−2.006 369 553 107 85(3)	0.000 089 149 638 7(7)	−2.006 601 516 715 010 67(3)	0.000 057 628 311 52
9 P	−2.006 156 384 652 86(5)	0.000 559 978 028(2)	−2.006 267 267 366 41(4)	−0.000 637 531 359(6)
9 D	−2.006 175 671 437 641(6)	−0.000 013 542 185(3)	−2.006 176 684 884 697(2)	0.000 004 306 538(6)
9 F	−2.006 173 406 897 324 6(8)	−0.000 001 099 967 1(3)	−2.006 173 412 365 043 0(7)	−0.000 001 019 651(2)
9 G	−2.006 172 991 627 586 3(2)	−0.000 000 298 267 2(1)	−2.006 172 991 643 665 0(3)	−0.000 000 298 019 8(1)
9 H	−2.006 172 891 903 619 14(2)	−0.000 000 104 002 2	−2.006 172 891 903 645 88(2)	−0.000 000 104 001 9
9 I	−2.006 172 860 732 382 57	−0.000 000 042 313 6	−2.006 172 860 732 382 60	−0.000 000 042 313 6(1)
9 K	−2.006 172 849 096 329 78	−0.000 000 019 151 6	−2.006 172 849 096 329 780	−0.000 000 019 151 6
10 S	−2.005 142 991 748 00(8)	0.000 064 697 214(3)	−2.005 310 794 915 611 3(2)	0.000 041 598 811 52
10 P	−2.004 987 983 802 22(4)	0.000 408 649 426 3	−2.005 068 805 497 8(1)	−0.000 463 433 718(8)
10 D	−2.005 002 071 654 250(6)	−0.000 009 947 506 0(6)	−2.005 002 818 080 232(8)	0.000 003 198 298(8)
10 F	−2.005 000 417 564 668 2(9)	−0.000 000 809 442(9)	−2.005 000 421 686 603 6(7)	−0.000 000 748 926 4(2)
10 G	−2.005 000 112 764 318 0(3)	−0.000 000 220 982(2)	−2.005 000 112 777 003 1(4)	−0.000 000 220 785(3)
10 H	−2.005 000 039 214 394 52(2)	−0.000 000 077 806 7	−2.005 000 039 214 417 41(2)	−0.000 000 077 806 2
10 I	−2.005 000 016 086 516 19	−0.000 000 032 059 0(1)	−2.005 000 016 086 516 22	−0.000 000 032 058 9(2)
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

Table 11.3. Eigenvalue coefficients ε_2 for helium.

State	$\varepsilon_2(n\,^1L)$	$\varepsilon_2(n\,^3L)$
1 S	−0.470 391 870(1)	
2 S	−0.135 276 864(1)	−0.057 495 847 9(2)
2 P	−0.168 271 22(7)	−0.204 959 88(1)
3 S	−0.058 599 3124(4)	−0.040 455 850 5(5)
3 P	−0.066 047 859(3)	−0.070 292 710(2)
3 D	−0.057 201 299(9)	−0.054 737 73(1)
4 S	−0.032 522 293(2)	−0.025 628 633 8(1)
4 P	−0.035 159 71(6)	−0.036 129 973(2)
4 D	−0.032 150 91(2)	−0.030 747 891(7)
4 F	−0.031 274 336(4)	−0.031 277 992 1(3)
5 S	−0.020 647 26(9)	−0.017 322 734 96
5 P	−0.021 847 6(3)	−0.022 166 61(9)
5 D	−0.020 510 1(2)	−0.019 706 2(2)
5 F	−0.020 013 498(6)	−0.020 016 561(4)
5 G	−0.020 003 560 8	−0.020 003 564 6
6 S	−0.014 261 796(4)	−0.012 411 399 1(3)
6 P	−0.014 902 86(9)	−0.015 033 58(5)
6 D	−0.014 199 4(2)	−0.013 707 27(1)
6 F	−0.013 896 984(2)	−0.013 899 22(3)
6 G	−0.013 891 179(6)	−0.013 891 184(8)
6 H	−0.013 889 619 1	−0.013 889 619 0
7 S	−0.010 438 2(2)	−0.009 304 443 3(3)
7 P	−0.010 818 6(2)	−0.010 879(2)
7 D	−0.010 405 09(3)	−0.010 085 212(1)
7 F	−0.010 209 2(3)	−0.010 210 7(3)
7 G	−0.010 205 61(5)	−0.010 205 61(5)
7 H	−0.010 204 590(2)	−0.010 204 587(2)
7 I	−0.010 204 276 7	−0.010 204 276 8
8 S	−0.007 968 944(3)	−0.007 224 770 5(3)
8 P	−0.008 211 7(5)	−0.008 248 7(6)
8 D	−0.007 950 7(4)	−0.007 731 59(2)
8 F	−0.007 815 9(3)	−0.007 817 0(2)
8 G	−0.007 813 563(1)	−0.007 813 568(3)
8 H	−0.007 812 855(4)	−0.007 812 859(5)
8 I	−0.007 812 642 9	−0.007 812 642 9
8 K	−0.007 812 563 0	−0.007 812 563 0
9 S	−0.006 282 5136(1)	−0.005 768 028 5(1)
9 P	−0.006 445 7(2)	−0.006 464 936 9(1)
9 D	−0.006 270 99(7)	−0.006 115 2(1)
9 F	−0.006 175 20(1)	−0.006 176 025 4(7)
9 G	−0.006 173 579 6(1)	−0.006 173 592(4)
9 H	−0.006 173 104(2)	−0.006 173 101(2)
9 I	−0.006 172 945 9(1)	−0.006 172 946 0(2)
9 K	−0.006 172 887 6	−0.006 172 887 6
10 S	−0.005 079 8362(8)	−0.004 709 453 0(1)
10 P	−0.005 197(1)	−0.005 206 7(1)
10 D	−0.005 072 4(4)	−0.004 958 0(8)
10 F	−0.005 001 76(2)	−0.005 002 386(2)
10 G	−0.005 000 55(2)	−0.005 000 55(2)
10 H	−0.005 000 193 5(2)	−0.005 000 193 5(1)
10 I	−0.005 000 080 3(4)	−0.005 000 081(1)
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

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

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	–2.005 142 991 747 919(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)

$-2.005\,000\cdots$ 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.

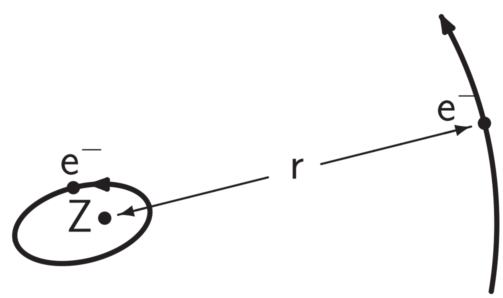

Figure showing the physical basis for a core-polarization model in which a Rydberg electron moves in the field generated by a polarizable core.