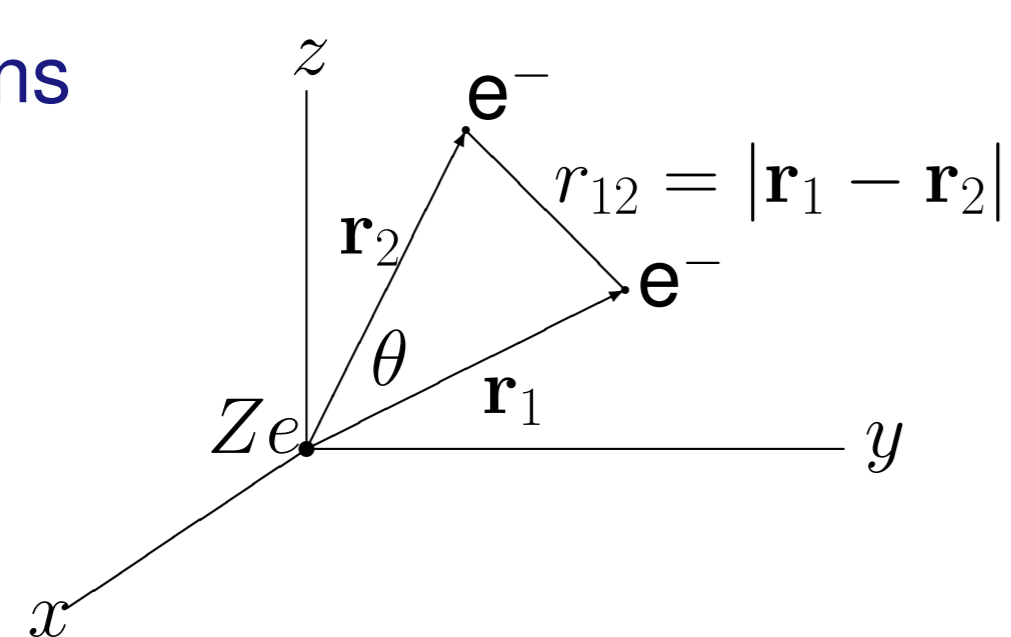


Introduction

Variational calculations readily produce high precision energies and wave functions for the ground state, but typically the accuracy rapidly deteriorates with increasing principal quantum number n . The current limit is $n = 10$ [1,2], except for S-states up to $n = 24$ [3]. We report the results of new variational calculations based on the use of triple basis sets in Hylleraas coordinates [4]. The basis sets are “tripled” in that each combination of powers i, j, k in basis functions of the form $r_1^i r_2^j r_{12}^k \exp(-\alpha r_1 - \beta r_2)$ is repeated three times with different nonlinear parameters α and β that are separately optimized to span different distance scales. Results are reported for the S- and P-states up to $n = 24$, including a comparison with high precision measurements for $n = 24$.

Calculations

Wave Functions



The Hamiltonian in atomic units is

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} - \frac{\mu}{M}\nabla_1 \cdot \nabla_2$$

where the last term is the mass polarization term, and μ is the electron reduced mass. Expand (for S-states)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i,j,k} a_{ijk} r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{i,j,k}^M(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2) \pm 1 \leftrightarrow 2$$

(Hylleraas, 1929), with $i + j + k \leq \Omega$, $\Omega = 1, 2, 3, \dots$.

Innovations for Rydberg States

I. Triple the basis set

If $\phi_{i,j,k}(\alpha, \beta) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2}$
then $\tilde{\phi}_{i,j,k} = a_1 \phi_{i,j,k}(\alpha_1, \beta_1) + a_2 \phi_{i,j,k}(\alpha_2, \beta_2) + a_3 \phi_{i,j,k}(\alpha_3, \beta_3)$
asymptotic intermediate inner correlation

II. Include the screened hydrogenic function

$$\phi_{SH} = \psi_{1s}(Z)\psi_{nL}(Z-1)$$

explicitly in the basis set.

III. Optimize the nonlinear parameters

$$\frac{\partial E}{\partial \alpha_t} = -2\langle \Psi_{tr} | H - E | r_1 \Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha_t) \pm r_2 \Psi(\mathbf{r}_2, \mathbf{r}_1; \alpha_t) \rangle$$

$$\frac{\partial E}{\partial \beta_t} = -2\langle \Psi_{tr} | H - E | r_2 \Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha_t) \pm r_1 \Psi(\mathbf{r}_2, \mathbf{r}_1; \alpha_t) \rangle$$

for $t = 1, 2, 3$, with $\langle \Psi_{tr} | \Psi_{tr} \rangle = 1$.

$\Psi(\mathbf{r}_1, \mathbf{r}_2; \alpha_t)$ = terms in Ψ_{tr} which depend explicitly on α_t .

For all states up to $n = 10$ and $L = 7$, see Drake and Yan, PRA **46**, 2378 (1992) and <http://drake.sharcnet.ca> for downloadable resources.

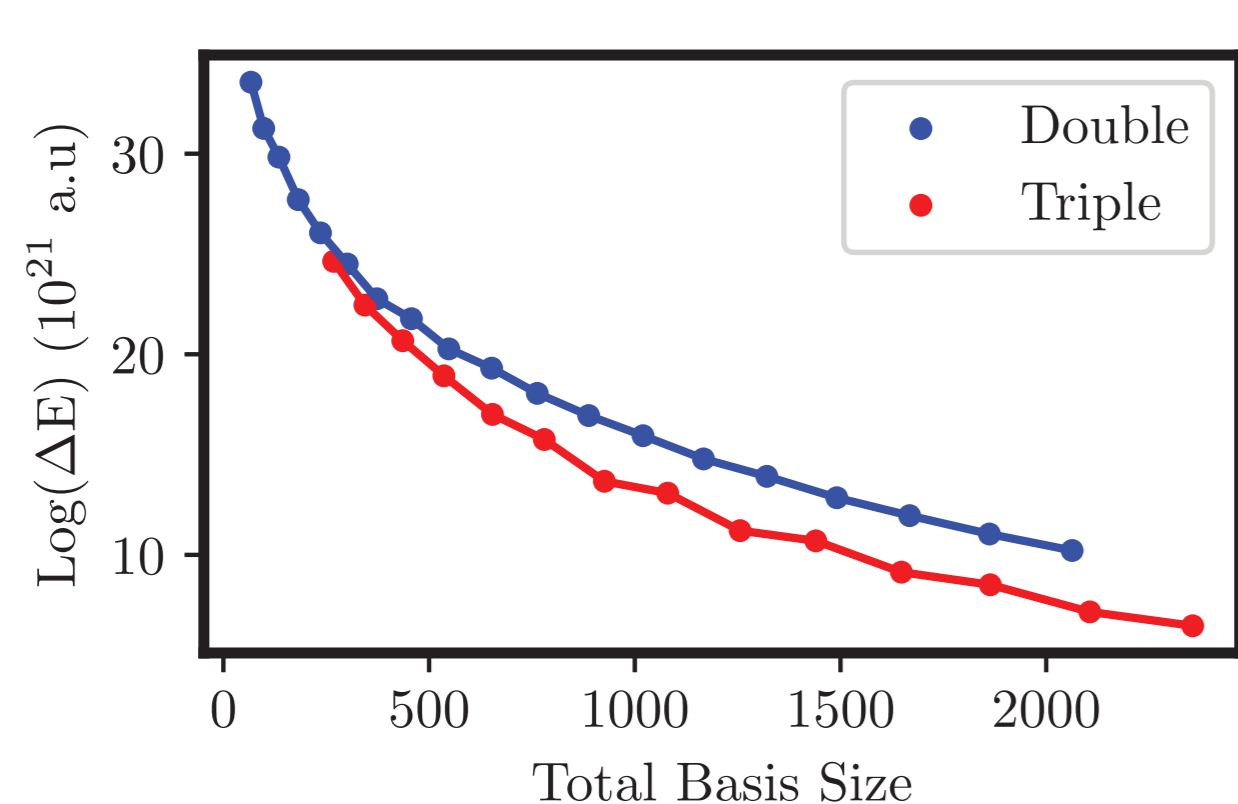
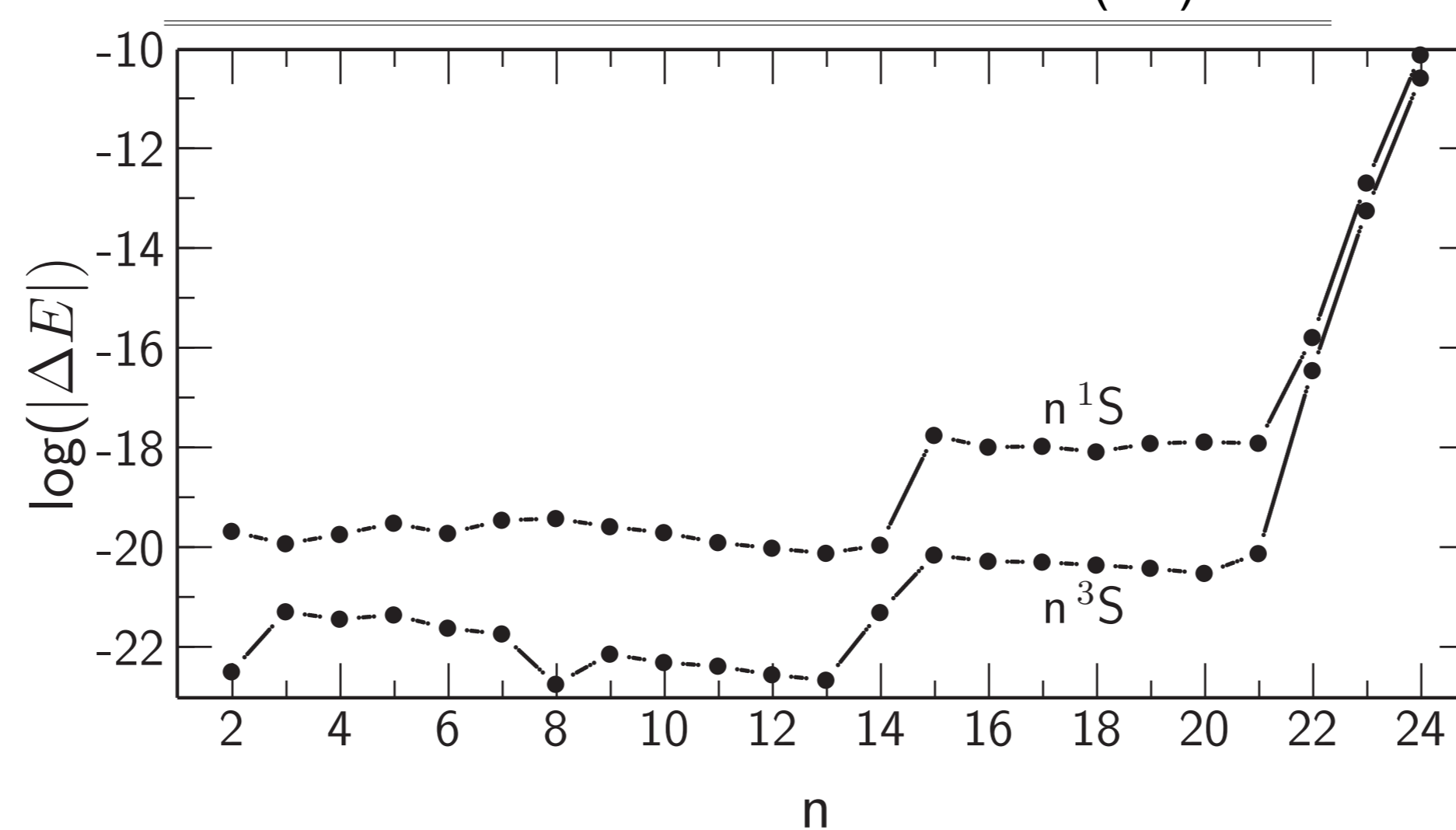


FIGURE 4.4: Comparison of energy difference vs total basis set size using a double and triple basis set for the $1s2s^1S$ state of helium with infinite nuclear mass.

Nonrelativistic Eigenvalues

Variational upper bounds for the $1sn s^1S$ states of helium.

n	E (a.u.)
11	-2.004 239 415 361 821 466 783 65(29)
12	-2.003 554 625 012 232 646 920(3)
13	-2.003 023 289 603 502 537 999 5(8)
14	-2.002 602 761 355 122 990 2003(6)
15	-2.002 264 241 270 263 477 839(70)
16	-2.001 987 713 181 956 783 067(8)
17	-2.001 758 915 080 010 318 109(8)
18	-2.001 567 462 439 135 929 869(10)
19	-2.001 405 648 670 772 638 268(15)
20	-2.001 267 657 216 551 211 353(10)
21	-2.001 987 713 181 956 783 067(8)
22	-2.001 046 310 060 125 804 014(15)
23	-2.000 956 772 051 472 370 03(6)
24	-2.000 878 254 279 512 826 01(22)



Comparison of present results with the ICI calculations of Nakashima et al. [3]. $\Delta E = E(\text{present}) - E(\text{ICI})$.

Variational eigenvalues for the Rydberg n^1P and n^3P states of helium with $n > 10$ (a.u.).

n	n^1P energy	n^3P energy
11	-2.004 123 191 922 332 652 537(30)	-2.004 183 903 199 590 642 324(3)
12	-2.003 465 252 704 885 798 265(21)	-2.004 183 903 199 590 642 324(3)
13	-2.002 953 093 958 149 784 866(2)	-2.002 989 859 764 908 816 319(11)
14	-2.002 546 625 370 190 968 007(8)	-2.002 576 056 426 625 768 993(13)
15	-2.002 218 647 104 088 301 579(1)	-2.002 242 571 222 150 326 423(24)
16	-2.001 950 177 973 979 340 796(1)	-2.001 969 887 403 296 967 040(22)
17	-2.001 727 645 999 910 516 844(1)	-2.001 744 075 191 087 356 05(11)
18	-2.001 541 138 760 913 624 73(75)	-2.001 554 976 940 232 726 628(17)
19	-2.001 383 280 102 341 609 732(15)	-2.001 395 044 604 295 124 904(54)
20	-2.001 248 489 450 687 613 307(28)	-2.001 258 574 692 820 423 853(37)
21	-2.001 132 481 733 017 529 657(90)	-2.001 141 192 656 477 678 529(90)
22	-2.001 031 922 552 162 285 513(90)	-2.001 039 497 912 816 701 274(90)
23	-2.000 944 185 877 955 806 76(38)	-2.000 950 814 760 962 146 15(18)
24	-2.000 867 180 846 170 111 25(14)	-2.000 873 014 566 616 659 34(31)

Relativistic Corrections

Relativistic corrections of $O(\alpha^2)$ are (in atomic units)

$$\Delta E_{\text{rel}} = \langle \Psi | H_{\text{rel}} | \Psi \rangle_J, \quad (1)$$

where Ψ is a nonrelativistic wave function and H_{rel} is the Breit interaction including the orbit-orbit, spin-orbit, spin-other-orbit, and spin-spin interactions, and including relativistic recoil corrections of order $\alpha^2 \mu/M$.

QED Corrections

The QED shift for a $1snL^1,3L$ state of helium has the form $E_{\text{QED}} = E_{L,1} + E_{M,1} + E_{R,1} + E_{L,2}$ where the main one-electron part is (in atomic units)

$$E_{L,1} = \frac{4Z\alpha^3 \langle \delta(\mathbf{r}_i) \rangle^{(0)}}{3} \left\{ \ln(Z\alpha)^{-2} - \beta(n^{1,3}L) + \frac{19}{30} + \dots \right\}$$

$\beta(n^{1,3}L) = \ln(k_0/Z^2 R_\infty)$ is the two-electron Bethe logarithm. For the $1snp^1P$ states,

$$\beta(n^1P) = 2.984 128 556 - \frac{0.004 920(5)}{n^3} + \frac{0.004 12(3)}{n^4} + \frac{0.001 03(3)}{n^5}$$

(G.W.F. Drake, Phys. Scr. **T95**, 22 (2001).)

Finite Nuclear Size Correction

In lowest order $\Delta E_{\text{mic}} = \frac{2\pi Z r_{\text{rms}}^2}{3} \langle \delta(\mathbf{r}_i) \rangle$, where $r_{\text{rms}} = R_{\text{rms}}/a_{\text{Bohr}}$, R_{rms} is the root-mean-square radius of the nuclear charge distribution, and a_{Bohr} is the Bohr radius.

Results

Contributions to the $1s24p^1P_1$ state ionization energies of ^4He

Contribution	Value (MHz)
Nonrelativistic (Enr)	5704 993.752 9760
1st. order mass pol. EM(1)	26.773 619(1)
2nd. order mass pol. EM(2)	-0.108 9079(2)
Relativistic (Erel)	-13.292 13(2)
Singlet-triplet mixing (Est)	0.002 2762
Relativistic finite mass (ERR)M	-0.006 7915
Relativistic recoil (ERR)X	0.003 5(7)
Finite nuclear size (Enuc)	0.000 0433
One-electron QED EL(1)	0.071 7540
Two-electron QED EL(2)	-0.040 2072
Higher-order QED	0.000 2(1)
Total	5704 980.350(1)

Comparison with Experiment [5]

From the quantum defect fit $E_n = E_I(2^1S_0) - \frac{R_{\text{He}}}{n^{*2}}$ where $n^* = n - \delta(n)$ is the effective principal quantum number

Comparison of theory and experiment for the $1s24p^1P_1$ ionization energy ^4He

Source	Value (MHz)
Theory	5704 980.350(1)
Expt., from QD fit	5704 980.312(95)
Expt., from $\nu(2^1S_0 - 24^1P_1)$	5704 980.352(40)*

* Gloria Clausen [5] and private communication.

Comparison of experiment and theory [6] for the ionization energies of the low-lying states of ^4He (MHz)

State	Experiment	Theory	Difference
2^3S_1	1152 842 742.640(32)	1152 842 742.231(52)	0.409(61)
2^3P_1	876 106 247.025(39)	876 106 246.611(16)	0.414(42)
3^3D_1	366 018 892.638(65)	366 018 892.691(23)	-0.053(69)
3^1D_2	365 917 748.688(34)	365 917 748.661(19)	0.027(38)

Summary and Discussion

• We have obtained the first high-precision eigenvalues for P-states with $n > 10$ up to $n = 24$, and better variational bounds for the S-states than the ICI calculations of Nakashima et al. [3].

• There is excellent agreement at $n = 24$ with the Zurich measurements of Clausen et al. [5], but a 10σ discrepancy of about 0.4 MHz remains for the 2^3S state of helium [6].

• Triple basis sets give improved accuracy by two or three orders of magnitude relative to double basis sets.

• Great numerical stability. Standard quadruple precision (~ 32 decimal digit) arithmetic gives energies accurate to 21 figures or more, at least up to $n = 15$.

On-line resources are available at drake.sharcnet.ca.

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