Rydberg States of the Helium Atom

JIA DENG, ANDREW T. B. GILBERT, PETER M. W. GILL
Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

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ABSTRACT: Using the recently introduced maximum overlap method and Hartree–Fock Perturbation Theory (HFPT), we compute Hartree–Fock (HF) wavefunctions for triplet $1s\,ns$ states of the helium atom. Comparison with near-exact results from Nakatsuji's free ICI method reveals that HF theory provides a simple route to accurate energies of these Rydberg states, especially for large n. © 2009 Wiley Periodicals, Inc. Int J Quantum Chem 109: 1915–1919, 2009

Key words: Rydberg states; excited states; helium; maximum overlap method; Hartree–Fock restoration

1. Introduction

During an illustrious career, Hirao has made many contributions to the discipline of quantum chemistry. One of his recent contributions concerns the development of systematic methods for improving the poor treatment of Rydberg and charge-transfer excitations afforded by time-dependent density functional theory (TD-DFT) with traditional functionals. Several years ago, he and his coworkers introduced [1] long-range-corrected density functional theory (LC-DFT) in which the Ewald [2–5] or erfgau [6, 7] partition is used to separate the Coulomb operator into a short-range part that is treated by density functional theory [8] and a long-range part that is treated using conventional wavefunction approaches [9]. As a result of Hirao's work, which has subsequently been adopted and adapted by several other groups, it is now possible to use TD-DFT to model both Rydberg and charge-transfer excitations with an accuracy comparable with that of valence excitations.

While Hirao was developing LC-DFT, Nakatsuji's group was introducing and exploring two impressive new approaches—the ICI method [10] and the free ICI method [11]—that yield near-exact solutions to the Schrödinger equation for small atomic and molecular systems. Recently, they have applied their approach to compute the ground-state energy of the helium atom to an astonishing 43 decimal digits [12] and also to obtain spectacularly accurate energies [13] for its singlet and triplet $1s\,ns$ states, for $n = 2, 3, \ldots, 24$.

In those states where $n \gg 1$, the electrons are spatially well separated and one might anticipate intuitively that they will be weakly correlated and that the Hartree-Fock (HF) method, which neglects such effects, may be an excellent approximation. Until recently, it has been difficult to test such predictions because traditional self-consistent field (SCF) algorithms struggle to locate highly excited solutions, tending instead to collapse to the lowest SCF

Correspondence to: P. M. W. Gill; e-mail: peter.gill@anu.edu.au

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solution with the same spin and spatial symmetry as the initial guess.

However, with the advent of the maximum overlap method (MOM) [14–16] and Hartree–Fock Perturbation Theory [17] for finding and refining excited-state solutions to SCF equations, one can now examine this prediction with relative ease. In the remainder of this article, we therefore investigate the accuracy with which the conceptually and computationally straightforward HF method approximates the exact energies of the 1*s* *ns* states of the helium atom, confining our attention to the triplet states to avoid the fundamental difficulties associated with the single-determinant description of open-shell singlets. Atomic units are used throughout.

2. Zeroth-order approximation

Before examining the performance of HF theory, it is illuminating to consider an even simpler independent particle model. In a 1*s* *ns* state where $n \gg 1$, the nuclear shielding by the inner electron is almost perfect and one can imagine electrons 1 and 2 occupying the He^+ 1*s* orbital and an H *ns* orbital, respectively.

This physical picture corresponds to partitioning the full Hamiltonian

$$H = -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}} \tag{1}$$

into a nonsymmetric, noninteracting zeroth-order part

$$H^{(0)} = \left(-\frac{\nabla_1^2}{2} - \frac{2}{r_1}\right) + \left(-\frac{\nabla_2^2}{2} - \frac{1}{r_2}\right) \tag{2}$$

and a perturbative correction

$$V = \frac{1}{r_{12}} - \frac{1}{r_2} \tag{3}$$

$H^{(0)}$ is a sum of two hydrogenic Hamiltonians and standard solutions yield

$$\Psi_n^{(0)}(\boldsymbol{r}_1, \boldsymbol{r}_2) = a(r_1)b_n(r_2) \tag{4}$$

$$E_n^{(0)} = -2 - 1/(2n^2) \tag{5}$$

where

$$a(r) = (\pi/8)^{-1/2}\exp(-2r) \tag{6}$$

$$b_n(r) = (n^5\pi)^{-1/2}\exp(-r/n)L_{n-1}^1(2r/n) \tag{7}$$

and L_n^m is an associated Laguerre polynomial [18]. The wavefunction (4) can be antisymmetrized, as appropriate for a triplet state, but the zeroth-order energy (5) is unaffected by this.

3. Hartree–Fock approximation

The Fock operator [19] for the 1*s* *ns* triplet state is

$$\boldsymbol{F} = -\frac{\nabla^2}{2} - \frac{2}{r} + \boldsymbol{J}_1 - \boldsymbol{K}_1 + \boldsymbol{J}_n - \boldsymbol{K}_n \tag{8}$$

and iterative diagonalization of $\boldsymbol{F}$ in a complete basis, using the MOM [15] to guide convergence, yields the exact HF energy E_n^{HF}.

We have used even-tempered Slater-type basis functions

$$\chi_k(\boldsymbol{r}) = \exp(-\alpha\beta^k r) \tag{9}$$

with $\alpha = 2$ and $\beta = 160/173$ and $k = 0, 1, \ldots, 69$. Although such a basis cannot be complete [20], we have found empirically that it is sufficiently large to yield energies for the triplet 1*s* *ns* states that are within a few nanohartrees of the HF limits for $n = 2, 3, \ldots, 24$. The basis is almost linearly dependent and we have therefore performed the HF calculations using extended precision in the Mathematica package [21].

Suppose that we use the zeroth-order orbitals (6) and (7) as the initial guesses for an HF calculation. The extent to which they will change during the SCF procedure depends on the extent to which the potentials assumed in the zeroth-order Hamiltonian $H^{(0)}$ are incorrect. This is illustrated for the $n = 10$ case in Figures 1 and 2.

The outer orbital $b_{10}(r)$ would remain unchanged if the inner electron shielded the nucleus perfectly

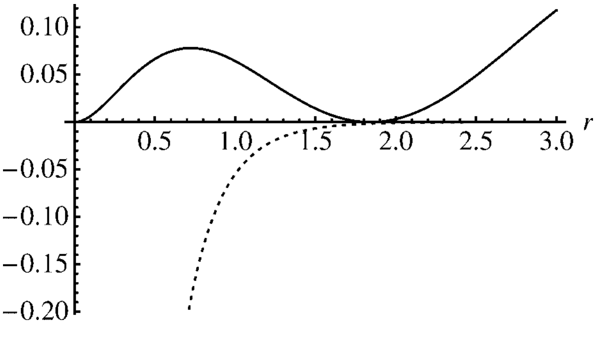

FIGURE 1. Radial density (×200) of the outer orbital $b_{10}(r)$ (solid) and $V_a(r) - 1/r$ (dotted).

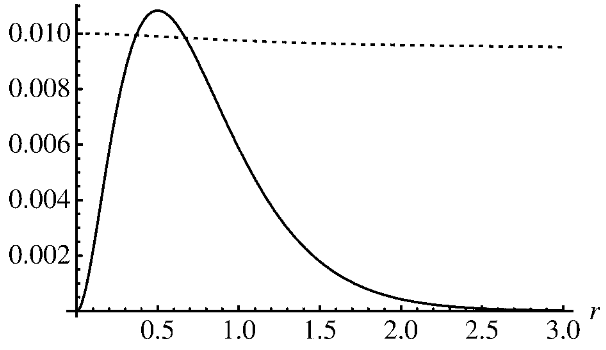

FIGURE 2. Radial density ($\times 0.01$) of the inner orbital $a(r)$ (solid) and $V_{10}(r)$ (dotted).

or, in other words, if the Coulomb potential

$$V_a(r) = \int \frac{a(\boldsymbol{r}')^2}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' \tag{10}$$

of the inner orbital were exactly $1/r$. However, as Figure 1 reveals, $V_a(r)$ significantly underestimates $1/r$ in a region close to the nucleus where there is a small component of the outer orbital's density. As a result of this imperfect shielding, the outer orbital contracts towards the nucleus during the SCF, leading to a slight lowering of the system's energy.

The inner orbital $a(r)$ would remain unchanged if the outer electron had no effect on it or, in other words, if the Coulomb potential

$$V_n(r) = \int \frac{b_n(\boldsymbol{r}')^2}{|\boldsymbol{r}-\boldsymbol{r}'|} d\boldsymbol{r}' \tag{11}$$

of the outer orbital is constant in the region where the inner electron is found. By constructing the Taylor series of $V_n(r)$ around $r = 0$, it can be shown that, near the nucleus, this potential is given by

$$V_n(r) = \frac{1}{n^2} - \frac{2r^2}{3n^3} + \frac{2r^3}{3n^3} - \cdots \tag{12}$$

and, as Figure 2 demonstrates, it is remarkably flat within the inner region. As a consequence, the inner orbital is essentially unaffected by the SCF and the optimized HF orbital remains extremely close to (6).

The inertness of the inner orbital greatly simplified our HF calculations because, by comparing our iterated energies with exact results for $n \leq 9$ from the Hartree–Fock Applet of Froese Fischer and Saparov [22], we found that its relaxation can be safely neglected for $n > 5$. We could then find the outer orbital by performing a single diagonalization of the orthogonalized reduced Fock operator

$$\boldsymbol{F} = -\frac{\nabla^2}{2} - \frac{2}{r} + \boldsymbol{J}_1 - \boldsymbol{K}_1 \tag{13}$$

in our large Slater basis. This "frozen core" approach is, in fact, a special case of the Hartree–Fock Perturbation Theory (HFPT) that we have recently developed [17].

4. Numerical results

In Table I, we compare the zeroth-order energies from Eq. (5), our Hartree-Fock energies and the exact energies from the free ICI method [13] for the lowest triplet 1*s* *ns* states of the helium atom. For convenience, we also give the resulting zeroth-order errors $\Delta_n^{(0)} = E_n^{(0)} - E_n^{\text{exact}}$ and correlation energies $E_{\text{corr}} = \Delta_n^{\text{HF}} = E_n^{\text{HF}} - E_n^{\text{exact}}$.

It is clear that the zeroth-order energies capture the essential behavior of the exact energies and that, as n grows they become increasingly accurate. At $n = 24$, the error of the zeroth-order energy is only 22 μE_{h} and the predicted ionization energy (868 μE_{h}) differs from the exact value (890 μE_{h}) by less than 3%.

It is also clear that the HF energies follow the exact energies very faithfully and that Δ_n^{HF} is typically almost two orders of magnitude smaller than $\Delta_n^{(0)}$. At $n = 24$, the error of the HF energy (i.e., the correlation energy) is less than 0.3 μE_{h} and the predicted ionization energy (889.6 μE_{h}) differs from the exact value (889.9 μE_{h}) by only 0.03%. Evidently, if one is interested in such highly excited 1*s* *ns* states, the simple Hartree-Fock approximation will be sufficiently accurate for many purposes.

Figure 3 shows log–log plots of the variation of $\Delta_n^{(0)}$ and Δ_n^{HF} with n, and reveals that both errors decay as $O(n^{-3})$. As we have discussed earlier, the zeroth-order errors result primarily from the neglect of the relaxation of the outer orbital and we note, therefore, that first-order perturbation corrections will not give useful improvements. However, almost all of the error disappears at the HF level and the tiny remaining error (which is simply the electron correlation energy) can probably be understood by a Drude or London model.

5. Concluding remarks

As this work was nearing completion, we discovered an article by Kuriyan and Pritchard [23]

TABLE I

0th-order, HF, and exact energies of triplet $1s\,ns$ states of He atom.

n	$-E_n^{(0)}$	$-E_n^{\mathrm{HF}}$	$-E_n^{\mathrm{exact}}$	$\Delta_n^{(0)}$	Δ_n^{HF}
2	2.125 000 00	2.174 250 78	2.175 229 38	5.0×10^{-2}	9.8×10^{-4}
3	2.055 555 56	2.068 484 95	2.068 689 07	1.3×10^{-2}	2.0×10^{-4}
4	2.031 250 00	2.036 436 42	2.036 512 08	5.3×10^{-3}	7.6×10^{-5}
5	2.020 000 00	2.022 582 62	2.022 618 87	2.6×10^{-3}	3.6×10^{-5}
6	2.013 888 89	2.015 357 34	2.015 377 45	1.5×10^{-3}	2.0×10^{-5}
7	2.010 204 08	2.011 117 58	2.011 129 92	9.3×10^{-4}	1.2×10^{-5}
8	2.007 812 50	2.008 419 01	2.008 427 12	6.1×10^{-4}	8.1×10^{-6}
9	2.006 172 84	2.006 595 90	2.006 601 52	4.3×10^{-4}	5.6×10^{-6}
10	2.005 000 00	2.005 306 75	2.005 310 79	3.1×10^{-4}	4.1×10^{-6}
11	2.004 132 23	2.004 361 69	2.004 364 70	2.3×10^{-4}	3.0×10^{-6}
12	2.003 472 22	2.003 648 33	2.003 650 63	1.8×10^{-4}	2.3×10^{-6}
13	2.002 958 58	2.003 096 67	2.003 098 47	1.4×10^{-4}	1.8×10^{-6}
14	2.002 551 02	2.002 661 30	2.002 662 73	1.1×10^{-4}	1.4×10^{-6}
15	2.002 222 22	2.002 311 68	2.002 312 84	9.1×10^{-5}	1.2×10^{-6}
16	2.001 953 13	2.002 026 69	2.002 027 64	7.5×10^{-5}	9.5×10^{-7}
17	2.001 730 10	2.001 791 33	2.001 792 12	6.2×10^{-5}	7.9×10^{-7}
18	2.001 543 21	2.001 594 71	2.001 595 38	5.2×10^{-5}	6.6×10^{-7}
19	2.001 385 04	2.001 428 77	2.001 429 34	4.4×10^{-5}	5.6×10^{-7}
20	2.001 250 00	2.001 287 45	2.001 287 93	3.8×10^{-5}	4.8×10^{-7}
21	2.001 133 79	2.001 166 10	2.001 166 52	3.3×10^{-5}	4.1×10^{-7}
22	2.001 033 06	2.001 061 14	2.001 061 50	2.8×10^{-5}	3.6×10^{-7}
23	2.000 945 18	2.000 969 73	2.000 970 04	2.5×10^{-5}	3.1×10^{-7}
24	2.000 868 06	2.000 889 65	2.000 889 92	2.2×10^{-5}	2.8×10^{-7}

which includes accurate HF calculations of $1s\,ns$ states of helium. Their energies agree well with ours for $n < 20$ but, beyond this, there are growing discrepancies and their values imply that the correlation energy Δ_n^{HF} begins to grow. Their HF energy for the $1s24s$ state, for example, implies the correlation energy $\Delta_{24}^{\mathrm{HF}} = 1.8\ \mu E_{\mathrm{h}}$, which is almost an order of magnitude too large. For this reason, we believe that our energies are more accurate than theirs.

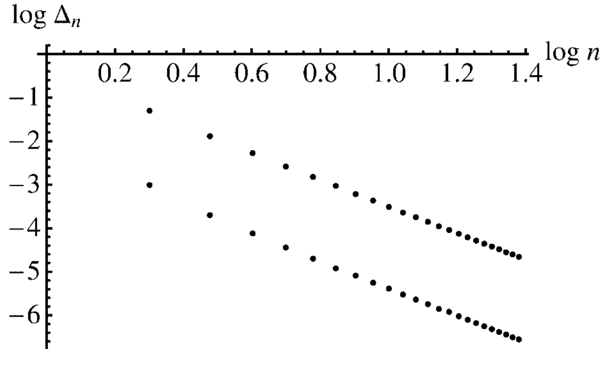

FIGURE 3. Variation of log $\Delta_n^{(0)}$ (upper) and log Δ_n^{HF} (lower) with log n.

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