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Confined helium: Excited singlet and triplet states

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ABSTRACT

Energies for the first four singlet and triplet S states of a helium atom confined at the center of an impenetrable sphere are reported. All calculations used explicitly correlated Hylleraas basis sets. The first triplet state is shown to lie below the first excited singlet state only when the confinement radius is greater than $0.988a_0$. A simple configuration interaction calculation was performed in parallel with Hylleraas calculation. The one-electron atomic orbitals of the configuration treatment provide insight into the physical concepts behind the numerical results of the Hylleraas treatment. This was particularly helpful in understanding the level crossing and avoided crossings observed with changing confinement radius.

1. Introduction

The effect of spatial confinement on atomic properties was first noted 100 years ago by Bohr in his classic 1913 paper [1]. In this work he noted that only twelve Balmer lines were observed in experiments using vacuum tubes while 33 lines were observed in some astronomical spectra. The new quantum theory was first used to study confinement of an atom in an impenetrable cavity by Michels et al. [2] who used it in 1937 to model the effects of pressure on the energy and polarizability of hydrogen. This was followed by the work of Sommerfeld and Welker [3] and Sommerfeld and Hartmann [4] who introduced solution of the confined hydrogen atom using confluent hypergeometric functions. From those seminal papers, confined systems have subsequently been studied by many workers using a variety of theoretical approaches. Confined atomic and molecular systems have recently been reviewed in two consecutive volumes of *Advances in Quantum Chemistry* [5] and the interested reader is referred to those reviews.

Most confined system calculations have used the Hartree–Fock method or density functional theory and have been restricted to the ground state. In the course of a study of electron correlation [6] using explicitly correlated expansions in Hylleraas coordinates [7], we realized that extension to excited singlet and triplet states was possible but significant reprogramming would be required to achieve a balance between precision and computational time. That reprogramming has been completed and the results are reported in this work for spherically symmetric S states.

Very recently Bhattacharyya et al. [8] published the energies for the first four excited singlet states of the confined helium-like systems with $Z = 1$–5. Their paper also contains a detailed description of previous results on the confined He problem. The present work is a confirmation of their calculated helium energies as well as an extension to the helium excited triplet states. New results that seem be physically important also are described here.

Hylleraas' approach provides an efficient method for two-electron calculations, but expansions in explicitly correlated basis sets have the disadvantage noted by Mulliken [9] that "the more accurate the calculations became, the more the concepts tended to vanish into thin air." Sometimes the traditional one-electron atomic orbitals provide more insight into the physical concepts behind the numerical results. To gain that insight we also performed a set of small elementary configuration interaction (CI) calculations that paralleled the Hylleraas energies. The CI treatment provides insight into the intersections and the avoided crossings that occur with changes in confinement.

2. Computational details

The approach of ten Seldam and de Groot [10] was followed through the development of the secular determinant. The wavefunctions were expansions of the form

$$\psi_N = \left[R - \frac{1}{2}(s-t)\right]\left[R - \frac{1}{2}(s+t)\right]e^{-\alpha s}\sum_{k=1}^{N} c_k s^{l_k} t^{m_k} u^{n_k}, \qquad (1)$$

where s, t and u are the Hylleraas coordinates [7] defined by

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Table 1
Selected energies in E_h for confined He. R is in a_0.

R/a_0	1^1S	2^1S	3^1S	4^1S	1^3S	2^3S	3^3S	4^3S
0.1	906.562423	1963.757922	2376.433159	3274.951095	2370.727023	3925.114157	4831.874925	5738.832217
0.5	22.741303	69.550421	80.065199	123.446146	78.820864	145.940357	176.363244	220.218568
1	1.015755	14.413766	15.127281	28.274446	14.359715	32.954387	38.515498	51.945225
					14.43401[b]			
1.5	−1.906956	4.272357	5.147166	10.057810	3.806768	13.035681	14.459349	20.361322
	−1.906957[a]							
2	−2.604038	0.946589	2.109932	4.201021	0.560251	6.373994	6.531128	9.890408
	−2.604038[a]				0.56961[b]			
2.5	−2.807835	−0.433214	0.821678	1.780156	−0.751657	2.998531	3.494876	5.345046
3	−2.872495	−1.114121	0.173325	0.645721	−1.370511	1.192269	1.987546	3.048669
	−2.872494[a]	−1.114121[a]			−1.36799[b]			
4	−2.900486	−1.717517	−0.458205	−0.286007	−1.874612	−0.497750	0.597762	1.009390
	−2.900486[a]		−0.458207[a]		−1.87331[b]			
5	−2.903412	−1.949762	−1.079197	−0.641430	−2.048044	−1.211382	0.019600	0.085991
	−2.903410[a]	−1.949761[a]	−1.079194[a]	−0.641647[a]	−2.04787[b]			
6	−2.903696	−2.050701	−1.460232	−0.735069	−2.117816	−1.562909	−0.683439	−0.257678
7	−2.903722	−2.097824	−1.675499	−1.031614	−2.148564	−1.754413	−1.123615	−0.406031
	−2.903721[a]	−2.098084[a]	−1.676567[a]	−1.034644[a]	2.14748[b]			
8	−2.903724	−2.120562	−1.799879	−1.294020	−2.162784	−1.866425	−1.395143	−0.747592
9	−2.903724	−2.129709	−1.854537	−1.393457	−2.169481	−1.935383	−1.571914	−1.066825
10	−2.903724	−2.133647	−1.880665	−1.443232	−2.172627	−1.979424	−1.691923	−1.288056
	−2.903724[a]	−2.139619[a]	−1.942677[a]	−1.942674[a]	−2.17146[b]			

[a] Ref. [8].
[b] Ref. [16].

$$s = r_1 + r_2, \qquad t = -r_1 + r_2, \qquad u = r_{12}, \tag{2}$$

and R is the radius of confinement.

The factors $[R - \frac{1}{2}(s \pm t)]$ are cutoff functions that insure the wavefunction goes to zero at the surface of the sphere of radius R, at the center of which the nucleus is placed. The wavefunctions included all terms with $l_k + m_k + n_k \leqslant 9$ subject to the requirement that $m_k =$ even for the singlet state and $m_k =$ odd for the triplet to ensure the required permutational symmetry of the spatial part of wavefunctions. The resulting wavefunctions thus included 125 basis sets. For $R \geqslant 2a_0$, α was determined by energy minimization (see below). For $R < 2a_0$ we found that setting $\alpha = 0$ changed the calculated energies only in the sixth decimal place.

The required integrals were evaluated as the sum of the two integrals

$$\int f\,d\tau = \int_0^R ds \int_0^s dt \int_t^s f\,du + \int_R^{2R} ds \int_0^{2R-s} dt \int_t^s f\,du, \tag{3}$$

as derived by Pan et al. [11]. A synopsis of Pan's method is provided in Appendix A. Using Pan's formulation decreased the computational time by 30% as compared to the method of ten Seldam and de Groot.

Since the introduction of the cutoff function effectively triples the number of terms in the wavefunction and each integral in the free atom calculation is replaced by the two integrals of Eq. (3), the number of integrals required for the confined atom calculation is increased by a factor of six as compared to a free atom wavefunction with the same size of basis sets. All calculations were coded in Maple 17 using 40 digit precision.

The ground and lowest triplet state were used to optimize α for a given multiplicity and R. The higher singlet and triplet states were then obtained by the linear variation method.

According to the Hylleraas–Undheim–MacDonald [12,13] theorem, the higher roots of the secular equation are upper bounds to the excited state eigenvalues.

To interpret the results within a more traditional orbital picture, we also used a small configuration interaction (CI) calculation in the basis of atomic orbitals of the He^+ system confined in a spherical cavity of radius R. The radial parts of the atomic orbitals can be described by confluent hypergeometric functions [2]. These functions were used for numerical integration (the step size $10^{-3}a_0$ is sufficient for stable results) by traditional methods of atomic calculations based on the Coulomb potential decomposition into Legendre polynomials and methods of angular momentum theory [14,15].

It is important here that for S states, electron configurations of the type $n\ell n'\ell'$ must use orbitals with the same angular momentum, $\ell' = \ell$. It is also worth mentioning that when one uses the basic configurations of the S type for triplet states, the permutational symmetry of the spatial parts of configurations requires an additional condition $n \neq n'$. Electron configurations of the form $n\ell^2$ are important only for singlet S states of two-electron system.

We stress that our CI calculations were used only to develop a qualitative description of the problem. There is usually no reason to compare these numerical energies with the much more accurate Hylleraas energies, as the quality of CI calculations is known to be inferior, especially for large ($R \sim 10a_0$) cavities. Nevertheless in terms of small-configurational functions one can use the more accurate results with the traditional constructions to separate numerical errors from real physical effects.

3. Results and discussion

Energies for the four lowest singlet and triplet S states were calculated over the range of R from $0.1a_0$ to $10a_0$. Selected energies from this work and from [8] and [16] are shown in Table 1. The wavefunction of Eq. (1) is competitive with the two-exponent wavefunction of [8] for $R \leqslant 5$ but is less accurate at large R and for more highly excited states. This is consistent with the idea that as R increases a second exponential term is necessary to accommodate radial correlation. However, an advantage of the single exponent expansion is that it remains numerically stable in the tight confinement region where the energy becomes positive.

For large R, just as for the free He atom, the lowest S states of the confined atom have configurations of the form $1sns$ and obey Hund's rules. The energies are ordered as

$$1^1S(1s^2),\ 1^3S(1s2s),\ 2^1S(1s2s),\ 2^3S(1s3s),\ 3^1S(1s3s), \ldots.$$

In the case of a spherical cavity of small radius the main contribution to the energy is given by the kinetic energy. The Coulombic