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Letter

Ground-state multiplicities of atoms and positive ions

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Abstract. A procedure is developed to establish the ground-state multiplicities for atoms with any number of electrons. The procedure is applied to two- and three-electron systems. The results are that all neutral and positive two- and three-electron atoms have singlet ($S = 0$) and doublet ($S = 1/2$) ground states, respectively.

Key words: Ground-state multiplicities – Atoms and ions

1 Introduction

Determination of ground-state multiplicities of atomic systems has long been a problem of interest [1]. It is widely accepted that the ground states of helium and other isoelectronic atoms (such as H^-, Li^+, and Be^{2+}) are singlet states. Support for this comes from experiment [2] and extremely large variational calculations [3–6]. Using the method of variance minimization, Kleindienst and Emrich [7] calculated very precise upper and lower bounds for the lowest singlet states of two-electron ions with atomic numbers between 1 and 10. Kleindienst and Degroot [8] followed this with a similar calculation for the lowest triplet states of those systems. Their results established that the singlet states are lower in energy than the triplet states for those systems.

This paper is concerned with a rigorous theoretical approach – rather than a computational approach – to this problem. The basic idea is as follows. If an upper bound to a state of given multiplicity is lower in energy than lower bounds of states with other multiplicities, then the former is the ground-state multiplicity of the system.

Our results support the findings of Kleindienst and coworkers and show that the same result holds for all atomic numbers. We also look at three-electron ions in detail and show that their ground states are of doublet multiplicity for all atomic numbers.

2 General relations

A rigorous upper bound to the ground-state energy, which appears similar to that of first-order perturbation theory, can be derived [9]. Let the electronic Hamiltonian be $H = H_0 + H'$, where H_0 is the sum of the electronic kinetic energy and nuclear attraction terms and H' contains the interelectronic repulsions. For an atomic system, let ψ_n and λ_n be the nth eigenfunction and eigenvalue of H_0. Then, if Λ_1 is the lowest eigenvalue of H, we have (by the variational theorem)

$$\begin{aligned}\Lambda_1 \le \langle\psi_n|H|\psi_n\rangle &= \langle\psi_n|H_0 + H'|\psi_n\rangle \\ &= \langle\psi_n|H_0|\psi_n\rangle + \langle\psi_n|H'|\psi_n\rangle \\ &= \lambda_n + \langle\psi_n|H'|\psi_n\rangle \ . \qquad (1)\end{aligned}$$

This gives an upper bound to Λ_1.

Now consider a particular spin subspace, with spin quantum number S. Let ${}^S\lambda_1$ be the lowest eigenvalue of H_0 and ${}^S\Lambda_1$ be the lowest eigenvalue of H in the spin-S subspace. Since the electron repulsion operator is positive definite, we know that

$${}^S\lambda_1 < {}^S\Lambda_1 \ . \qquad (2)$$

This gives an explicit lower bound to ${}^S\Lambda_1$.

If we could show that $\lambda_n + \langle\psi_n|H'|\psi_n\rangle < {}^S\lambda_1$ we would know that the ground state does not occur in the spin-S subspace, for we would have

$$\Lambda_1 \le \lambda_n + \langle\psi_n|H'|\psi_n\rangle < {}^S\lambda_1 < {}^S\Lambda_1 \ . \qquad (3)$$

The eigenstates of the full Hamiltonian need not be known in this analysis. All terms are easily calculable from the exactly known hydrogenic states.

We now investigate the relationships in Eq. (3) with a general Hamiltonian.

Let $\mathscr{X}$ be the spatial (spin-free) Hilbert space, $\mathscr{F}$ be the full (spatial plus spin) Hilbert space, $\mathscr{S}$ be the spin-S subspace of $\mathscr{F}$, and $\mathscr{A}$ be the antisymmetrized subspace of $\mathscr{S}$. For a symmetric spin-free Hamiltonian, H, it is well known that the eigenstates in $\mathscr{X}$ can be used to generate the eigenstates in $\mathscr{A}$; however, we must be sure that all the eigenstates in $\mathscr{A}$ can be generated. To show this, we present for completeness and clarity some simple

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and previously known results which use the fact that a symmetric Hamiltonian, H, and the antisymmetrizer, A, commute (i.e. $AH = HA$).

Theorem 1. Given a symmetric spinless Hamiltonian, H, all its eigenstates in $\mathscr{A}$ can be generated from its eigenstates in $\mathscr{X}$.

Proof. We establish a chain of lemmas stating that all the eigenstates in one space can be generated from the eigenstates in another space – thus we generate eigenstates in $\mathscr{A}$ by cycling through the spaces $\mathscr{X}$, $\mathscr{F}$, $\mathscr{S}$, and finally $\mathscr{A}$ itself in that order. Going from $\mathscr{X}$ to $\mathscr{F}$ requires writing the eigenstates in $\mathscr{F}$ as a linear combination of the eigenstates in $\mathscr{X}$ (plus orthonormal states added for completeness) multiplied by linear combinations of orthonormal spin functions. Going from $\mathscr{F}$ to $\mathscr{S}$ and then from $\mathscr{S}$ to $\mathscr{A}$ results from the fact that $\mathscr{A}$ is a subspace of $\mathscr{S}$, which is in turn a subspace of $\mathscr{F}$. Thus, we are only eliminating solutions outside the subspaces.

Theorem 2. For a spin-free Hamiltonian, when eigenstates in $\mathscr{X}$ are used to generate eigenstates in $\mathscr{A}$, the energy eigenvalue, λ, is the same for both problems.

Proof. Using theorem 1, we can write any eigenfunction as linear combinations of degenerate spin eigenfunctions and degenerate spatial eigenfunctions in $\mathscr{X}$ with eigenvalue λ. Omitting indices for simplicity and assuming that $A(\sum Q \sum \Phi)$ is normalized, we have

$$\begin{aligned}
E &= \left\langle A\left(\sum Q \sum \Phi\right) \middle| H \middle| A\left(\sum Q \sum \Phi\right)\right\rangle \\
&= \left\langle A\left(\sum Q \sum \Phi\right) \middle| HA\left(\sum Q \sum \Phi\right)\right\rangle \\
&= \left\langle A\left(\sum Q \sum \Phi\right) \middle| AH\left(\sum Q \sum \Phi\right)\right\rangle \\
&= \left\langle A\left(\sum Q \sum \Phi\right) \middle| A\left(\sum Q \sum H\Phi\right)\right\rangle \\
&= \left\langle A\left(\sum Q \sum \Phi\right) \middle| A\left(\sum Q \sum \lambda\Phi\right)\right\rangle \\
&= \lambda\left\langle A\left(\sum Q \sum \Phi\right) \middle| A\left(\sum Q \sum \Phi\right)\right\rangle \\
&= \lambda \ .
\end{aligned}$$

Thus the energy eigenvalue is equal to the eigenvalue of any of the degenerate spatial components of the wavefunction. An identical argument shows that the spin eigenvalue is equal to the common spin eigenvalue of the spin components of the wavefunction.

3 Two-electron atoms

The spatial and spin components of two-electron wavefunctions are separable; therefore, we can limit our attention to symmetric spatial functions when working in the singlet ($S = 0$) subspace (the spin functions are antisymmetric) and to antisymmetric spatial functions when working in the triplet ($S = 1$) subspace (where the spin functions are symmetric).

We know that $\lambda_1 = -Z^2$, which is the sum of the eigenvalues of two 1s orbitals (we can ignore the spin part by theorem 2), and $\langle \psi_1 | H' | \psi_1 \rangle = \langle 1s1s | H' | 1s1s \rangle = 5Z/8$. Thus,

$$\Lambda_1 \leq -Z^2 + 5Z/8 \ .$$

We also know that H_0 gives lower bounds to the true eigenvalues of $H_0 + H'$ since H' is positive definite. For the triplet ($S = 1$) subspace, we know that the sum of the eigenvalues of the 1s and 2s orbitals ($-Z^2/2 - Z^2/8$) is a lower bound to the lowest eigenvalue. If $\Lambda_1 < -Z^2/2 - Z^2/8$, we then have that the lowest eigenvalue in the whole Hilbert space is less than all the eigenvalues in the triplet subspace, and must therefore belong to the singlet subspace.

We do not know Λ_1, but we know an upper bound: $\Lambda_1 \leq -Z^2 + 5Z/8$. Thus, to show that Λ_1 is not in the triplet subspace, we must find when ${}^0\lambda_1 = -Z^2 + 5Z/8 < -Z^2/2 - Z^2/8 = {}^1\lambda_1$ is satisfied. A little manipulation reveals that this is true when $Z > 5/3$. This shows that for $Z \geq 2$, all two-electron atoms have a singlet ground state. For $Z = 1$, Hill [10] proved that only one bound singlet state exists and that there are no bound triplet states; thus, the ground state for H^- is a singlet state. Combining Hill's result with ours shows that all two-electron atoms have singlet ($S = 0$) ground states.

4 Three-electron atoms

For three-electron atoms, there are again only two spin states: the doublet ($S = 1/2$) and the quartet ($S = 3/2$). Unfortunately, the wavefunctions can no longer be factored into products of spatial and spin components. A complete set of orthonormal spin eigenfunctions is [11]

$$\begin{array}{lll}
S = 1/2 & 1/\sqrt{6}(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) & 1/\sqrt{2}(\alpha\beta\alpha - \beta\alpha\alpha) \\
 & 1/\sqrt{6}(2\beta\beta\alpha - \beta\alpha\beta - \alpha\beta\beta) & 1/\sqrt{2}(\beta\alpha\beta - \alpha\beta\beta)
\end{array}$$

$$\begin{array}{lll}
S = 3/2 & 1/\sqrt{3}(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha) & \alpha\alpha\alpha \\
 & 1/\sqrt{3}(\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta) & \beta\beta\beta \ .
\end{array}$$

To find the lowest energy eigenvalue of the repulsionless Hamiltonian in the spin subspaces (for use in Eq. 3), we must know which one-electron orbitals are used in the wavefunction. By theorem 2, we know that the energy eigenvalue is independent of the spin parts; however, the antisymmetrizer annihilates certain products of spin and spatial functions.

If a, b, and c denote different orthonormal spatial orbitals and Q denotes a spin eigenfunction, then in the doublet space $A(aaaQ)$ vanishes, and both $A(aabQ)$ and $A(abcQ)$ are nonzero. In the quartet space, $A(aaaQ)$ and $A(aabQ)$ both vanish; only $A(abcQ)$ survives. Thus, the lowest eigenvalue for the doublet subspace, ${}^{1/2}\lambda_1 = -Z^2/2 - Z^2/2 - Z^2/8 = -9Z^2/8$, comes from the 1$s1s2s$ spatial term (or equivalently replace 2s with a 2p orbital) and the lowest eigenvalue for the quartet subspace, ${}^{3/2}\lambda_1 = -Z^2/2 - Z^2/8 - Z^2/8 = -6Z^2/8$, comes from the 1$s2s2p$ spatial term.

To show when (if ever) Eq. (3) holds, we work with the function $1s1s2s\alpha\beta\alpha$, which is a solution of the repulsionless Hamiltonian in the doublet subspace and gives a nonzero function when it is antisymmetrized. In Eq. (3), we require the integral

$$\begin{aligned}\langle\psi_n|H'|\psi_n\rangle &= \langle A(1s1s2s\alpha\beta\alpha)|1/r_{12}+1/r_{13}\\ &\quad +1/r_{23}|A(1s1s2s\alpha\beta\alpha)\rangle \ .\end{aligned}$$

An upper bound will suffice for this. We therefore neglect the exchange terms and use

$$\begin{aligned}&\langle 1s1s2s|1/r_{12}+1/r_{13}+1/r_{23}|1s1s2s\rangle\\ &\quad = Z(5/8+17/81+17/81) = Z(677/648) \ .\end{aligned}$$

Substituting our values into Eq. (3), we obtain

$$\begin{aligned}\Lambda_1 &\le {}^{1/2}\lambda_1 + \langle\psi_1|H'|\psi_1\rangle\\ &= -\frac{9}{8}Z^2 + \frac{677}{648}Z < -\frac{6}{8}Z^2\\ &= {}^{3/2}\lambda_1 < {}^{3/2}\Lambda_1 \ .\end{aligned}$$

Rearranging, we find that the middle inequality is true when $Z > 677/243$. Thus, we can conclude that all three-electron atoms with $Z \ge 3$ have doublet ($S = 1/2$) ground states.

5 Conclusion

This same procedure can be extended to any number of electrons and is very simple (although tedious for many electrons) because it relies on the hydrogenic eigenfunctions only. This simplicity, however, makes the bounds on the eigenvalues very poor. It is expected that as the number of electrons increases, the generality of the method will suffer because of this. Indeed, for the four-electron case, this method shows only that atoms with $Z \ge 5$ (i.e. positively charged) have $S = 0$ ground states, and a specific calculation must be done for $Z = 4$ (neutral beryllium). This is because the lowest singlet and triplet states are relatively close in energy [2].

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