

Some remarks on the two-electron atom

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Abstract

New, approximate, two-electron wavefunctions are introduced for the two-electron atoms (cations), which account remarkably well for the ground-state energies and the lowest- excited states (where available). A new scheme of electronic configurations is also proposed for the multi-electron atoms.

Following Bohr,[1] the electronic structure of the atoms is currently described by means of the central self-consistent field, based on the Hartree-Fock equations.[2]·[3] Although this mean-field doctrine has long served the interpretation of the atomic spectra,[4] its central assumption of single-electron wavefunctions has never been given an a priori legitimacy. In fact, correlated ground-state wavefunctions have been worked out in great detail for the *He* atom and, generally, for the two-electron atom.[5]–[7] In spite of the fact that these very elaborate techniques, which are variational in essence, produce impressively accurate numerical results for the ground-state energies, they look, however, rather arbitrary, and can not be extended easily to multi-electron atoms. We introduce in this paper new, approximate, two-electron wavefunctions for the two-electron atom, which give the ground-state and the lowest-excited states energies with an accuracy which may be regarded as being remarkable for the simplicity of the approach. We propose also a new general scheme of electronic configurations, which may constitute a reasonable starting point for understanding the nature of the electronic structure of the multi-electron atoms.

If not specified otherwise, we use throughout this paper the atomic units $a_H = \hbar^2/me^2 = 0.53 \text{ \AA}$ (Bohr radius) and $e^2/a_H = 27.2 \text{ eV}$ (twice the rydberg), which render the square of the electron charge $e^2 = 1$; in addition, we set the Planck's constant $\hbar = 1$, so that the electron mass $m = 1$. We start with considering two electrons, denoted by 1 and 2, placed at \mathbf{r}_1 and, respectively, \mathbf{r}_2 in the Coulomb field of a nuclear charge Z . We neglect the center-of-mass corrections, the spin-orbit coupling, as well as all the other relativistic corrections; they can be treated perturbationally. Under these assumptions the hamiltonian of the two-electron atom is given by

$$H = \frac{1}{2}p_1^2 + \frac{1}{2}p_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad , \quad (1)$$

where $\mathbf{p}_{1,2}$ are the momenta of the two electrons. We shall treat first the electron affinity of hydrogen, *i.e.* the ground-state of the H^- anion ($Z = 1$), and thereafter we shall proceed to the atoms (cations) with $Z \geq 2$.

If we put $\mathbf{r}_1 = -\mathbf{r}_2$ in (1) (for $Z = 1$) we get a one-particle hamiltonian for a particle of mass 1/2, moving in a Coulomb field of charge 3/2; its ground-state energy is $E_0^{(0)} = -9/16 = -15.3 \text{ eV}$, which amounts to an electron affinity $A^{(0)} = 1.7 \text{ eV}$. This value is close to the experimental value $A = 0.76 \text{ eV}$. [8] The zeroth order approximation $E_0^{(0)}$ must be corrected by higher-order

contributions of the Coulomb repulsion $V = 1/|\mathbf{r}_1 - \mathbf{r}_2|$ between the two electrons. For a fixed \mathbf{r}_1 we can see that this Coulomb repulsion describes, to the first order of approximation, harmonic oscillations of $\mathbf{r}_2 = (r_2, \theta_2, \varphi_2)$ along θ_2 , around $\mathbf{r}_2 = -\mathbf{r}_1$. The corresponding harmonic-oscillator potentials have, however, various curvatures, and we should define an average potential. Setting to describe the small oscillations of \mathbf{r}_2 by the displacements $\boldsymbol{\rho}$, *i.e.* putting $\mathbf{r}_2 = -\mathbf{r}_1 + \boldsymbol{\rho}$, we may expand the Coulomb repulsion V as

$$V = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{2r} + \frac{\rho}{4r^2} P_1(\cos \theta) + \dots \quad (2)$$

where $r = |\mathbf{r}_1| = |\mathbf{r}_2|$, P_1 is the Legendre polynomial of the first rank, and θ is the angle between $\boldsymbol{\rho}$ and \mathbf{r}_1 . We define the average potential \bar{V} by $\bar{V} = (\bar{V}^2)^{1/2}$, where the average in parenthesis is taken over all the orientations of $\boldsymbol{\rho}$, so that, we get in the first approximation

$$\bar{V} = \frac{1}{2r} + \frac{\rho^2}{48r^3} + \dots \quad (3)$$

The first term in (3) has already been included in computing the zeroth order approximation; the second term in (3) is a harmonic-oscillator potential, which is completely determined by replacing r by its average value over the zeroth order ground-state $\bar{r} = 2$. We obtain therefore the harmonic-oscillator frequency $\varpi = (24r^3)^{-1/2} = 1.96 \text{ eV}$, and the ground-state energy corrected by the zero-point oscillations $E_0 = E_0^{(0)} + \frac{1}{2}\varpi = -14.32 \text{ eV}$; this amounts to an electron affinity $A = 0.72 \text{ eV}$ which is in excellent agreement with the experimental value 0.76 eV . We remark that the oscillations of the second electron are along θ_2 , so that they correspond to only one degree of freedom.

For $Z \geq 2$ we define $r = \min(r_1, r_2)$ and $R = \max(r_1, r_2)$ and separate the hamiltonian (1) as follows:

$$H = H_Z + H_{Z_1} + V \quad (4)$$

$$H_Z = \frac{1}{2}p^2 - \frac{Z}{r} \quad (5)$$

$$H_{Z_1} = \frac{1}{2}P^2 - \frac{Z_1}{R} \quad (6)$$

$$V = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} - \frac{1}{R} \quad (7)$$

where $Z_1 = Z - 1$ and \mathbf{p} , \mathbf{P} are the momenta of the electrons placed at \mathbf{r} and, respectively, \mathbf{R} . This separation corresponds to the classical concept of screening. The two hamiltonians H_Z and H_{Z_1} have a hydrogen-like energy spectrum; the ground-state wavefunction is given by $\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = C_0 \Psi_{100}^{(Z)}(\mathbf{r}) \Psi_{100}^{(Z_1)}(\mathbf{R})$, where $\Psi_{100}^{(Z, Z_1)}$ are the corresponding ground-state wavefunctions of the hydrogen-like atom (normalized to unity) and C_0 is a normalization constant. This wavefunction corresponds to an electron configuration which may be denoted by $(100) \times (100)$, and has the energy

$$E_0^{(0)} = -\frac{Z^2}{2} - \frac{Z_1^2}{2} = -Z^2 + Z - 1/2 \quad (8)$$

One can check easily that this energy is very close to the actual ground-state energy of the two-electron atoms (cations). For example, we have $E_0^{(0)} = -68 \text{ eV}$ as compared with the experimental value $E_0^{\text{exp}} = -79 \text{ eV}$ for the He atom ($Z = 2$), and $E_0^{(0)} = -176.8 \text{ eV}$, as compared with $E_0^{\text{exp}} = -198 \text{ eV}$ for the Li^+ cation. The remaining interaction V can be written as

$$V = \sum_{l=1}^{\infty} \frac{r^l}{R^{l+1}} P_l(\cos \Omega) = \sum_{l=1}^{\infty} \sum_{m=-l}^l \frac{4\pi}{2l+1} \cdot \frac{r^l}{R^{l+1}} \cdot Y_{lm}(\theta, \varphi) Y_{lm}^*(\Theta, \Phi) \quad (9)$$

where P_l are the Legendre polynomials, Y_{lm} are the spherical harmonics, Ω is the angle between \mathbf{r} and \mathbf{R} , and $\mathbf{r} = (r, \theta, \varphi)$, $\mathbf{R} = (R, \Theta, \Phi)$. This interaction can, in principle, be treated perturbationally. However, the main contribution to this interaction comes from those space regions where $r \sim R$, so that the perturbation series converges extremely slowly. Consequently, we shall account for its main effect in another way.

Analyzing its expression given by (7) we see easily that V has a minimum value at $r = R$ and $\Omega = \pi$; this value is given by $V = -1/2r$. We shall assume, therefore, that the ground-state wavefunction given above is slightly distorted in such a way as to allow the second electron to take full advantage of this minimum of energy. This amounts to correcting $E_0^{(0)}$ by $\bar{V} = -1/2\bar{r}_0$, where \bar{r}_0 is the average value of the electron distances to the nucleus $\bar{r}_1 = \bar{r}_2 = \bar{r}_0$ over the hydrogen-like configuration (100) \times (100) given above. We give here the expression of this average radius

$$\begin{aligned} \bar{r}_0 = C_0^2 \cdot 16(ZZ_1)^3 \int dr_2 \cdot r_2^2 \cdot \left(\int_0^{r_2} dr_1 \cdot r_1^3 \cdot e^{-2Zr_1} \cdot e^{-2Z_1r_2} + \right. \\ \left. + \int_{r_2}^{\infty} dr_1 \cdot r_1^3 \cdot e^{-2Z_1r_1} \cdot e^{-2Zr_2} \right) . \end{aligned} \quad (10)$$

The ground-state energy is therefore

$$E_0 = E_0^{(0)} - 1/2\bar{r}_0 , \quad (11)$$

and we remark that $-1/2\bar{r}_0$ is a classical correction, corresponding to the principle of minimization of the energy for the ground-state. In particular, we note that the first-order correction of V , as given by (9), within the quantum-mechanical perturbation theory vanishes for the ground-state. Within the present picture the ground-state of the two-electron atom looks as being made of two electrons, one moving inside, and the other outside an imaginary sphere, and changing continuously their places through $\mathbf{r}_1 \cong -\mathbf{r}_2$. Remark that further corrections like zero-point oscillations around $\mathbf{r}_2 = -\mathbf{r}_1$ done for the H^- anion would be inappropriate here since the second electron moves everywhere (independently) outside the $r_2 = r_1$ sphere in the Coulomb field of charge Z_1 . The normalization constants C_0 , the average radii \bar{r}_0 and the ground-state energies E_0 given by (11) are computed in *Table 1* for $Z = 2$ through 11, and compared with the experimental values of the ground-state energies E_0^{exp} . One can see that the agreement is very good, the errors being less than 0.6%.

Within the present approximation the full wavefunctions of the ground-state of the two-electron atom, including the spin degrees of freedom, may be written (up to a normalization constant) as

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \times \left\{ \begin{array}{l} \Psi_{100}^{(Z)}(\mathbf{r}_1)\Psi_{100}^{(Z_1)}(\mathbf{r}_2) , r_1 < r_2 , \\ \Psi_{100}^{(Z)}(\mathbf{r}_2)\Psi_{100}^{(Z_1)}(\mathbf{r}_1) , r_1 > r_2 , \end{array} \right\} , \quad (12)$$

for the spin-singlet state, and

$$\Psi_0(\mathbf{r}_1, \mathbf{r}_2) = \left\{ \begin{array}{l} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) \\ \beta(1)\beta(2) \end{array} \right\} \times \left\{ \begin{array}{l} \Psi_{100}^{(Z)}(\mathbf{r}_1)\Psi_{100}^{(Z_1)}(\mathbf{r}_2) , r_1 < r_2 , \\ -\Psi_{100}^{(Z)}(\mathbf{r}_2)\Psi_{100}^{(Z_1)}(\mathbf{r}_1) , r_1 > r_2 , \end{array} \right\} , \quad (13)$$

for the spin-triplet state, where α , β are the spin-up and spin-down wavefunctions. The wavefunctions written above are antisymmetric, such as to satisfy the Pauli exclusion principle. Within the present approximation these wavefunctions correspond to the same energy, so that the para- and the ortho-atoms are degenerate. However, a closer inspection of (12), for example, tells us that the orbital of this wavefunction, though continuous at $\mathbf{r}_1 = \mathbf{r}_2$ has discontinuous derivatives at these points; and, similarly, the orbital wavefunction given by (13) is discontinuous at $\mathbf{r}_1 = \mathbf{r}_2$.

The exact orbitals will be continuous, and will have continuous derivatives at $\mathbf{r}_1 = \mathbf{r}_2$, which implies that the spin-triplet orbital will have a sudden variation on passing through zero at $\mathbf{r}_1 = \mathbf{r}_2$. This indicates that the ortho-atom will have a higher energy, so that we may conclude that the ground-state corresponds to a spin-singlet (para-atom).

We remark also that the wavefunctions given by (12) and (13) are, essentially, correlated wavefunctions, or genuine two-electron wavefunctions. Indeed, one may define, for example,

$$\varphi_2(1) = \left\{ \begin{array}{l} \Psi_{100}^{(Z)}(\mathbf{r}_1) \quad , \quad r_1 < r_2 \quad , \\ \Psi_{100}^{(Z_1)}(\mathbf{r}_1) \quad , \quad r_1 > r_2 \quad , \end{array} \right\} \quad , \quad (14)$$

and write the spin-singlet orbital of the ground-state as $\varphi_2(1)\varphi_1(2)$; in spite of certain appearances, this is a correlated, two-electron wavefunction, since, for example, according to its definition (14), the wavefunction $\varphi_2(1)$, as function of \mathbf{r}_1 , depends on \mathbf{r}_2 .

We pass now to the lowest-excited states of the two-electron atoms (cations). with nuclear charge $Z \geq 2$. It is easily to check that, to the zeroth order approximation, the lowest-excited states correspond to the hydrogen-like configurations $(100) \times (200)$ and $(100) \times (21m)$, *i.e.* the wavefunctions are $\Psi_{100}^{(Z)}(\mathbf{r})\Psi_{200}^{(Z_1)}(\mathbf{R})$ and $\Psi_{100}^{(Z)}(\mathbf{r})\Psi_{21m}^{(Z_1)}(\mathbf{R})$, according to the notations introduced above. The corresponding energy is

$$E_1 = -\frac{Z^2}{2} - \frac{Z_1^2}{8} = -\frac{5Z^2}{8} + \frac{Z}{4} - \frac{1}{8} \quad . \quad (15)$$

Indeed, one can check easily that the other alternative, corresponding to the configurations $(200) \times (100)$, $(21m) \times (100)$, has a much higher energy. One can also check straightforwardly that the energies given by (15) are already very close to the experimental values, as one can see in *Table 2*, for $Z = 2$ (*He*) and $Z = 3$ (*Li⁺*); the experimental values for larger Z , where available, have no longer been included in *Table 2* as they correspond clearly to much higher-excited states; for example, $E^{\text{exp}} = -119.6 \text{ eV}$ for the *Be²⁺* cation,[8] while (15) gives $E = -248.2 \text{ eV}$ for $Z = 4$. In *Table 2* there have also been included the normalization constants C_1 for the configuration $(100) \times (21m)$, as well as the average radii \bar{r}_1 over this state for $Z = 2$ through 11. We shall remark, first, that a correction of the type $-1/2\bar{r}_1$, as in the case of the ground-state energy, is not appropriate here, since the excited states are only stationary states, but they do not, of course, minimize the energy, as the ground-state does. One may check that including $-1/2\bar{r}_1$ in the energy computed above would, indeed, result in worse numbers, *i.e.* there would be a larger discrepancy with respect to the experimental values. Secondly, we remark that although the two configurations $(100) \times (200)$ and $(100) \times (21m)$ are degenerate in this approximation, the former is not orthogonal to the ground-state, as the latter is. An orthogonalization procedure will push this state toward higher energies, so that the lowest-excited state corresponds very closely to the $(100) \times (21m)$ configuration. Thirdly, we may also remark that an improved approximation to the lowest excited level may proceed by standard perturbation calculations applied to the interaction V given by (9), keeping in mind that we have to include those states that conserve the total angular momentum. In the case of $(100) \times (21m)$ this is $L = 1$, and the interaction V couples this state to $(21m) \times (100)$, $(21m) \times (200)$, $(32m') \times (21m)$, etc. As we have said, the perturbation series converges, however, very slowly, as the main contributions come from $r \sim R$. And finally, let us remark that the continuity of the two-particle orbitals at $\mathbf{r}_1 = \mathbf{r}_2$, and of their derivatives, brings an additional splitting in energy between the spin-singlet and spin-triplet states, as discussed above.

Obviously, the above scheme of electronic configurations may be extended to multi-electron atoms. For example, for an atom with N electrons, we may set up (to the zeroth order approximation) the configuration $(nlm) \times (n'l'm') \times (n''l''m'') \times \dots$ etc, where each paranthesis denotes a

hydrogen-like orbital corresponding, respectively, to a nuclear charge Z , $Z_1 = Z - 1$, $Z_2 = Z - 2$, etc, up to $Z_{N-1} = Z - (N - 1)$. The remaining interaction of the type V given in (7) can then be minimized classically for the ground-state, according to the procedure described above. Similar electronic configurations may also be used as starting points for the excited states. Obviously, we have, in this picture, correlated, multi-electronic wavefunctions, though each electron moves in a central field, corresponding, however, to different nuclear charges. One may infer that, within this picture, the atoms are more "rarefied", leading to increased transition probabilities, as compared with those corresponding to all electrons moving in a unique nuclear charge. Of course, the first thing to be done for checking the validity of such a scheme of electronic configurations would be that of trying to account for the periodicity of the chemical elements, i.e. the counterpart of the closed-shell assumption of the self-consistent field model of the atom.

References

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Table 1

Z	C_0	\bar{r}_0	$-E_0(eV)$	$-E_0^{\text{exp}}(eV)$
2 (He)	0.795	1.177	79.554	78.98
3 (Li^{1+})	0.856	0.650	197.713	198
4 (Be^{2+})	0.889	0.452	370.087	371.5
5 (B^{3+})	0.910	0.347	596.809	599.3
6 (C^{4+})	0.925	0.282	877.91	881.6
7 (N^{5+})	0.935	0.237	$1.213 \cdot 10^3$	$1.218 \cdot 10^3$
8 (O^{6+})	0.943	0.205	$1.603 \cdot 10^3$	$1.609 \cdot 10^3$
9 (F^{7+})	0.949	0.180	$2.048 \cdot 10^3$	$2.055 \cdot 10^3$
10 (Ne^{8+})	0.954	0.161	$2.546 \cdot 10^3$	$2.556 \cdot 10^3$
11 (Na^{9+})	0.958	0.145	$3.099 \cdot 10^3$	$3.11 \cdot 10^3$

Table 2

Z	C_1	\bar{r}_1	$-E_1(eV)$	$-E_1^{\text{exp}}(eV)$
2 (He)	0.709	2.907	57.8	59.16
3 (Li^{1+})	0.712	1.558	136	138.98
4 (Be^{2+})	0.714	1.092	248.2	—
5 (B^{3+})	0.715	0.853	394.4	—
6 (C^{4+})	0.717	0.708	574.6	—
7 (N^{5+})	0.718	0.610	788.8	—
8 (O^{6+})	0.718	0.539	$1.037 \cdot 10^3$	—
9 (F^{7+})	0.719	0.485	$1.319 \cdot 10^3$	—
10 (Ne^{8+})	0.719	0.444	$1.635 \cdot 10^3$	—
11 (Na^{9+})	0.720	0.410	$1.986 \cdot 10^3$	—

Table captions

Table 1

The normalization constants C_0 , the average radii \bar{r}_0 , the ground-state energies E_0 as given by (11) and the experimental values E_0^{exp} of the ground-state energies[8] for the ground-state configuration $(100) \times (100)$ of the two-electron atoms (cations), as functions of the nuclear charge Z .

Table 2

The normalization constants C_1 , the average radii \bar{r}_1 , the energies E_1 as given by (15) for the lowest-excited states corresponding to the configuration $(100) \times (21m)$, as well as the experimental values E_1^{exp} for the lowest levels[8] of the two-electron atoms (cations), as functions of the nuclear charge Z ; the experimental values for $Z > 3$ have not been included as they correspond to higher excited levels.