PHYSICAL REVIEW A VOLUME 45, NUMBER 3 1 FEBRUARY 1992

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First-order perturbation theory and resonance energies of two-electron atoms

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(Received 9 August 1991)

A simple expression for the energies of a class of doubly excited states derived from first-order perturbation theory is compared with recent results based on large numerical calculations for H^- and He. It concerns $_{n'}(K,T)_n^{A\,2S+1}L^\pi$ states with $A=+1$, $L=0$, or 1, $K=n-1-T$, $T=\frac{1}{2}[1-\pi(-1)^S]$. (Lin's standard notation is used.) This expression involves both intrashell and intershell cases.

PACS number(s): 31.15.+q, 31.20.−d, 34.80.−i, 31.50.+w

Neglecting spin, the nonrelativistic two-electron atomic Hamiltonian is

$$H=H_0+1/|\mathbf{r}-\mathbf{r}'|\ ,$$

where $H_0=h+h'$ and $h(h')$ is a hydrogenic Hamiltonian:

$$h=p^2/2-Z/r\ .$$

If the interelectronic repulsion term $1/|\mathbf{r}-\mathbf{r}'|$ is treated as a perturbation, the ground-state energy E within first-order perturbation theory is (see, e.g., Ref. [1])

$$E=-Z^2+(\tfrac{5}{8})Z\ .$$

Atomic units are used throughout this paper. The experimental values for $Z=3,2,1$ are about -7.28, -2.9, -0.5276, respectively. The relative error therefore rises from about -2% for Li^+ ($Z=3$), about -5% for He ($Z=2$), up to about -29% for H^- ($Z=1$). The present Brief Report is concerned with the comparison of a simple perturbative approach for the energies of some highly doubly excited states with respect to recent elaborated nonperturbative numerical results.

The unperturbed Hamiltonian H_0 has the $O(4)\times O(4)$ dynamical symmetry of two hydrogenic Hamiltonians. As a result, the degeneracy degree pertaining to the bound states of H_0 is equal to $(nn')^2$ where n and n' are the principal quantum numbers associated with each electron. On one hand, this large degeneracy degree for n, n' large makes first-order perturbation theory difficult to implement. On the other hand, one can expect that first-order perturbation theory will be particularly suitable for the particular set of highly doubly excited states with wave functions sharply confined in a region where the interelectronic angle is nearly equal to π. Such a geometric configuration clearly minimizes the interelectronic repulsion and thus favors a perturbative approach. It is a general property of highly degenerate systems that eigenvectors with wave functions well localized in some regions of configuration space can be constructed. Thus, for the hydrogen atom, one can construct within the n^2-dimensional subspace ($n\gg1$) states well localized on one side only of the nucleus, corresponding to configuration-space wave functions separable in parabolic coordinates and suitable for the zero-order Stark effect. More generally, it is possible to construct stationary states localized on a classical elliptical orbit [2] which correspond to O(4) coherent states. Returning now to the two-electron problem, it is possible to construct within a subspace of fixed total orbital angular momentum L ($n\gg L$, $n'\gg L$) eigenstates of H_0 whose configuration-space wave functions are strongly concentrated at an interelectronic angle θ equal to π. Explicit construction has been given in Refs. [3,4]. It amounts essentially to diagonalizing B^2, the square of the difference of the two monoelectronic Runge-Lenz vectors. This diagonalization is achieved using only angular momentum algebra. For a fixed value of the total angular orbital momentum L, the eigenvector of B^2 with largest eigenvalue corresponds to the smallest mean value of $\cos(\theta)$. For the intrashell cases ($n=n'$) the mean value of $\cos(\theta)$ for the vectors that diagonalize B^2 has been obtained explicitly in Ref. [5]. The general expression (i.e., the expression valid for both the intrashell and the intershell cases) has recently been obtained [Eqs. (A6), (41), and (A9) of Ref. [6]]. This general expression is rather complicated but simplifies for those vectors corresponding to the largest eigenvalue of B^2:

$$\langle\cos(\theta)\rangle=-1+\frac{(n-1)^2+(n'-1)^2+nn'-1+L(L+1)(n-1)(n'-1)/(n+n'-2)}{[nn'(n+n'-2)]}\ .$$

TABLE I. ${}_{n'}(K=n-2,\ T=1)_n^{+}\ {}^1P^o$ states of H^- and He. These states are labeled ${}_n(0)_{n'}^{+}$, by Sadeghpour [12]. The first two columns correspond to n,n'. The third and fourth columns give, for H^- and He respectively, the percentage of accuracy of Eq. (2) with respect to the results obtained from large numerical calculations. Specifically, they correspond to $100(x-y)/y$ where x is the perturbative result given by Eq. (2) of the present paper and y is the value calculated by Sadeghpour [12]. Blank spaces correspond to the cases where y has not been calculated.

n	n'	H^-	He
4	4	8.18	4.61
4	5	4.16	4.54
4	6	−1.75	2.84
4	7		1.63
4	8		0.78
4	9		0.23
4	10		−0.10
4	11		−0.30
4	12		−0.42
4	13		−0.49
5	5	3.85	2.30
5	6	2.94	3.16
5	7	−0.98	2.31
5	8		1.56
5	9		0.89
5	10		0.39
5	11		0.04
5	12		−0.21
5	13		−0.36
6	6	0.94	1.89
6	7	0.96	3.01
6	8	−1.16	2.86
6	9	−3.18	1.34
6	10		0.88
6	11		0.47
6	12		0.15
6	13		−0.09
7	7	0.09	1.03
7	8	0.09	1.26
7	9	−1.26	2.81
7	10	−2.83	2.19
7	11		1.67
7	12		1.32
7	13		1.03
8	8	−1.42	0.03
8	9	−0.94	−0.78
8	10	−1.72	0.41
8	11	−2.83	0.75
8	12		0.70
8	13		0.50
9	9	−2.00	0.03
9	10	−1.62	0.55
9	11		1.76
10	10	−2.51	−0.48
10	11	−3.47	−0.58
10	12		−0.12
11	11	−2.93	
11	12	−2.42	
12	12	−3.05	
12	13	−1.98	

It is seen that this expression decreases when decreasing L, and for a fixed value of L, goes to minus unity as both n and n' increase.

It has recently been conjectured [6] on the basis of an analysis of the two-electron atomic problem within the framework of the O(4,2) group, that the resonance positions of the states with $L=0$ and mean values of $\cos(\theta)$ very near to -1 correspond to those of the Hamiltonian H_1:

$$H_1=H_0+1/(r+r') \tag{1}$$

in the subspace where $l=l'=0$. The ratio $[1/(r+r')]/[(Z/r)+Z/r')]$ is less than or equal to $1/(4Z)$ whatever the r,r' values are. The maximum value occurs for $r=r'$. The situation is thus favorable for $1/(r+r')$ to be considered as a perturbation, especially if n and n' are very different. An estimate of the mean value of $1/(r+r')$ was then obtained [6] on the basis of classical mechanics and the corresponding first-order perturbative energies are [6]

$$E(n,n')=-\tfrac{1}{2}Z^2(1/n^2+1/n'^2) + Z\{\tfrac{1}{2}s-[(2/nn')+d\arcsin(d/s)]/\pi\}\ , \tag{2}$$

where

$$s\equiv(1/n^2)+(1/n'^2)\ , \quad d\equiv(1/n^2)-(1/n'^2)\ .$$

For the intrashell case ($n=n'$), Eq. (2) simplifies

$$E(n,n)=-(Z/n)^2+Z[1-(2/\pi)]/(n^2)\ ,$$

a result previously obtained by Dmitrieva and Plindov [7,8].

It remains to specify more precisely the states for which Eq. (2) should actually be relevant. Two electron states are labeled according to the now standard notation of Lin [9] by ${}_{n'}(K,T)_n^{A\ 2S+1}L^{\pi}$. The superscript A is not an independent quantum number [9]. The channels with $A=+1$ have been found [9] to have the lowest energies, i.e., energies nearest to those of the unperturbed Hamiltonian H_0. The perturbative approach should therefore

TABLE II. ${}_{n'}(K=n-1,\ T=0)_n^{+}\ {}^1S^e$ states of H^- and He. Same as in Table I, but y is from Koyama *et al.* [13] and Fukuda, Koyama, and Matsuzawa [14].

n	n'	H^-	He
3	3	1.63	3.06
3	4	−0.36	3.48
4	4	−0.34	1.67
4	5	−0.34	2.51
5	5	−2.11	0.50
5	6	−1.41	1.02
6	6	−2.86	0.09
6	7		0.73
7	7	−3.94	−1.04
7	8	−3.17	−1.21
8	8	−4.54	
8	9	−4.12	
9	9	−4.91	
9	10	−4.32	

be relevant to the case $A=+1$. A is related to S, T, and π by the relation [9] $A=\pi(-1)^{S+T}$ if $K>L-n$. For a fixed value of L, the energies are minimum for K maximum, $K=n-1-T$, corresponding to the smallest mean value of $\cos(\theta)$. Thus T should be equal to zero for even singlet states and odd triplet states, and equal to 1 for even triplet states or odd singlet states. The two possibilities for the pair S,π when T,K,A,n,n',L are fixed correspond to near degenerate states and are called T doubling [9]. Although Eq. (2) was introduced for the case of zero total orbital angular momentum L, it can also be conjectured if for small L values ($L=1,2$) with a dropping accuracy as L increases whereas n,n' remain fixed. The starting point of the conjecture in Ref. [6] was an approximation of Eq. (74) of Ref. [10]. It can indeed be seen that this approximation is still valid, although to a lesser degree of accuracy, if L remains small . This is compatible with the fact that adiabatic potential curves in hyperspherical coordinates are nearly degenerate for different values of L and identical channel quantum numbers K,T,A [9]. A rotational band structure [11,9] then appears as L increases from its minimum value T. The present perturbative approach should not be sufficiently accurate to distinguish between the first two rotational levels. To summarize, Eq. (2) is expected to be best relevant for the states labeled

$$_{n'}(K=n-1-T,\ T=\tfrac{1}{2}[1-\pi(-1)^{S}])_{n}\,{}^{2S+1}(L=0\text{ or }1)^{\pi} \tag{3}$$

with large n',n values. Extensive calculations based on the hyperspherical method concerning both intrashell and intershell ${}^{1}P^{o}$ energies of H^{-} and He were quite recently published by Sadeghpour [12]. The results of these numerical calculations for those states compatible with the labeling described just above ($L=1$, $\pi=-1$, $S=0$, $T=1$, $K=n-2$) are compared with the results of Eq. (2) in Table I for H^{-} and for He. To our knowledge, there exist no such extensive calculations involving both the intrashell and intershell cases for the $L=0$ case. The most extensive results we have found are those of Koyama *et al.* [13] and Fukuda, Koyama, and Matsuzawa [14] ($L=0$, $\pi=1$, $S=0$, $T=0$, $K=n-1$). The relative accuracy of Eq. (2) with respect to the values calculated from the hyperspherical coordinate method [13,14] are reported in Table II. For the intrashell case ($n=n'$) there are also the numerical results of Rost and Briggs based on a molecular approach [15] ($L=0$, $\pi=1$, $S=0$, $T=0$, $K=n-1$). Relative accuracy of Eq. (2) with respect to these results is reported in Table III. From Tables I–III it appears that the energies given by Eq. (2) tend to be too low for small n,n' values and too high for large n,n' values, especially for S states. Further numerical results are needed to analyze the large-n behavior in Table III; in view of the present results, it is reasonable to expect an accuracy better than about 3% for He and better than about 10% for H^{-}.

TABLE III. $_{n}(K=n-1,\ T=0)_{n}^{+}\,{}^{1}S^{e}$ states of H^{-} and He. Same as in Table I, but y is from Rost and Briggs [15].

n	n'	H^{-}	He
3	3	6.10	3.06
4	4	7.19	1.63
5	5	−2.27	0.75
6	6	−3.38	0.19
7	7	−4.20	−0.22
8	8	−4.70	−0.50
9	9	−5.37	−0.78
10	10	−5.86	−0.98
11	11		−1.15
12	12		−1.28
13	13		−1.38
14	14		−1.47
15	15		−1.57

To summarize, Eq. (2) relies on two major points: first, the conjecture [6] that the Hamiltonian H_1 [Eq. (1)] in the subspace $l=l'=0$ is relevant for the energies of the states labeled by Eq. (3) if both n and n' are large; second, the use of first-order perturbation for doubly excited states of this Hamiltonian with $l=l'=0$. In our opinion, the accuracy of the present result [Eq. (2)] is better than one could expect, especially for H^{-}. At present it cannot be excluded that the agreement with much more elaborate calculations [12–15] is fortuitous, but in our opinion the present comparisons give support to the conjecture of Ref. [6]. Finally, convenient and often more accurate, at least on a given energy range, double Rydberg formulas have been given in the literature for the intrashell ($n=n'$) cases (see, e.g., Refs. [16–19]). Rydberg-Rydberg formulas or two-electron formulas have been proposed for the intershell cases [12,20,21]. Equation (2) should be regarded as a first estimate which does not involve any fitted parameters. It also has the advantage that both intrashell and intershell cases are treated on the same footing.

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