Quantum mechanical study of He atom

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In this paper we study the various physical properties and processes for two-electron atoms, principally helium. A two-electron atom is a system of three interacting particles, a problem even extremely difficult to analyze within classical mechanics (because the motion of the electrons is non-integrable and chaotic). Since the mass of the nucleus is much larger than that of the electron, the nuclear motion may be ingorned (or treated perturbatively) and the problem reduces to two interacting particles moving in an external potential. This is still a non-trival problem both in classical mechanics and quantum mechanics due to the non-separability of the three-body Coulomb problem. The effect of the non-separability becomes evident in a doubly excited state, in which both electrons are excited.

Atomic theory has proceeded traditionally along the microscopic approach of formulating the Schrödinger equation for a set of electrons and nuclei and trying to solve it as accurately as possible. A major part of the effort of atomic theory since the birth of quantum mechanics has been devoted to dealing with the electron-electron correlations perturbatively. Based on the independent particle approximation a few different perturbative approaches, such as many-body perturbation theory (MBPT) and the configuration-interaction (CI) method have been developed. However, there are two particular characters for the doubly excited state. First, the electron-electron interaction is comparable to the electron-nucleus interaction. This strong electron-electron correlation leads to the breakdown of the independent particle approach. Secondly, the energy of the doubly excited state is higher than the ground state energy of a He^+ ion plus a free electron. Such a doubly excited state would therefore quickly disintegrate into a He^+ ion and a free electron. That means the state lies in the continuous spectrum, but is not a discrete state. Evidence of a primary role of the correlations in shaping the states of an electron pair emerged in 1963 [1] from the first observation of doubly excited states of He using synchrotron

radiation. Theoretical explanation by Cooper, Fano and Prats [2] indicated that a complete understanding of these new states requires a fundamental departure from the conventional independent particle model.

A variety of theoretical approaches have been reported recently [3] to study the doubly excited states of the two-electron atom. Roughly speaking, these methods may divide into two categories according to the theoretical framework they use. The first is based on the base of the independent-electron model, the configuration interaction (CI) method is an example of this type. This type of approach suffers from very slow convergence and it is also quite difficult to incorporate the coutinuum states. The second uses the trial pseudostate basis set, for example the variational method and the close-coupling method. As we know, unphysical psuedo-resonances can get created with this method and each state has to be treated separately. It may also be more difficult to generalize them to high-lying doubly excited states.

The hyperspherical coordinate method has played a prominent role for describing strong electron-electron correlations. Introduced to atomic physics by Macek [4], the method helped visualize effective potential energies and account for characteristic correlation patterns of doubly excited states [5]. In this representation, the two electrons are treated equally as a single entity that has a hyperradius R measuring the 'size' of the electron pair and a hyperangle α describing the degree of radial correlation. The success of the hyperspherical approach lies in the approximate separability of the hyperradial motion in R from the more rapid angular momtion in $\Omega = (\alpha, \hat{r}_1, \hat{r}_2)$. Thus it is possible to employ a quasi-separable approximation, adiabatic approximation. This approximation method has given us a very clear picture as to how electrons correlate at different R and also has connected to a new simple classification scheme to describe these states. However, there is strict limitation on the extention of adiabatic approximation to high-lying doubly excited states. This is due to the fact thst there are more and more avoided crossings for higher adiabatic channels. Hence the channel couplings cannot be ingored or treated perturbatively. For high-precision computations, the coupled equations should be solved instead of employing adiabatic approximation.

Attempts to improve the adiabatic calculation by coupling the adiabatic channels [6] have been tried but without success. This may be due to following reasons. First, the suggested composite basis functions [7], which consist of hyperspherical harmonics and analytic channel functions, were widely used to construct the adiabatic channel functions. This composite basis displays linear dependence because

of its overcompleteness and non-orthogonality, severely hampering the diagonalization procedure and producing unphysical eigenvalues. This makes it inappliable to accurate calculations. Secondly, the non-adiabatic coupling between the adiabatic channels varies rapidly near a localized avoided crossing and is numerically very difficult to handle. Finally, in the asymptotic region (that is at large R) it is more appropriate to represent the system using the independent particle coordinates. Although the hyperspherical coordinates are very close to the independent particle coordinates at large R, the small difference between them introduces a small but ever-present radial coupling between the adiabatic channels. It has been shown [8] that it takes the coupling of an infinite number of adiabatic channels at large R to reproduce the independent particle states in the asymptotic region.

We wish to develop an accurate and general *ab initio* method for two-electron atoms. In order to develop an accurate and unified theoretical treatment of discrete, doubly excited, and continuum spectra, we turn the hyperspherical method into a competitive computational scheme. First we present an efficient and accurate numerical scheme for setting up the hyperspherical basis functions which dictate the accuracy of the whole method [9]. The diabatic-by-sector method is employed to numerically integrate the hyperspherical close-coupling equations. It is well-known that the hyperspherical coordinates are inadequate for representing the asymptotic boundary condition for one-electron ionization or detachment. Therefore in the asymptotic region, we employ the so-called 2-dimensional matching procedure to match the hyperspherical solutions to the asymptotic ones expressed in the separable electron coordinates (r_1, r_2). Then we deduce the correct K-matrix as well as total wavefunctions of the atom. The proposed sequence of procedures can treat highly correlated bound, continuum and doubly excited states in a unified fashion. For the dipole transition, the wavefunctions of initial and final states are obtained in a consistent way. Hence the dipole transition matrix (D-matrix) can be calculated easily [10]. From the K-matrix and D-matrix, all the physical quantities (resonance energy, width, phase-shift, oscillator strength, electron-impact spectrum and photoionization spectrum, etc.) can be deduced. The convergence of the method is monotonic as a function of the number of channels included. It is free of the problems encountered by those methods which exploit pseudostates.

We have examined the efficiency and accuracy of our hyperspherical close-coupling method using He as a test case [9, 10]. By calculating various physics quantities and comparing with other theoretical and experimental results our HSCC

method has proved very efficient and accurate. Exploring high-lying doubly excited states is important for consolidating our present understanding of the electron-electron correlation as well as for studying the correspondence between classical mechanics and quantum mechanics. However, this is an extremely demanding task for the existing computational methods because of the large unmber of open channels. Owing to the development of the fast and monotonically convergent diabatic basis functions, we have not encounterd any practical difficulties that prevent us from studying the high-lying doubly excited states [11]. As an example, we compare our calculated photoionization spectrum below N=5 and 6 threshold with the experimental one [12] in the figure. We see that every experimental findings are satisfactory reproduced.

Some problems remained to be studied. For example, the correspondence of the classical orbits with the quantum mechanical spectrum. The present method may be extended into several future directions, for instance, to atoms/ions with two active electrons outside a closed shell core.
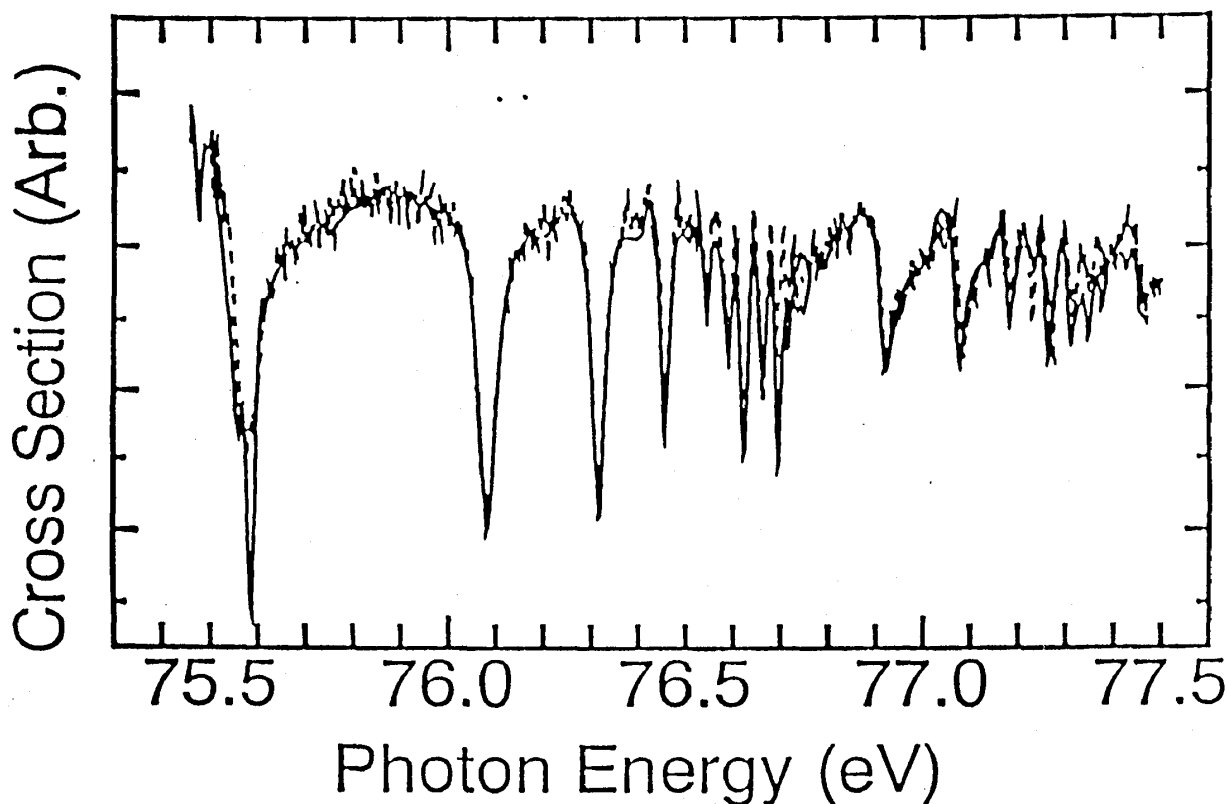

Figure ...1.: The calculated photoionization spectrum of He are compared with the experimental one. Solid curve: calculated spectrum; dashed curve: experimental one.

REFERENCES

[1] R. P. Madden and K. Codling, Phys. Rev. Lett. **10**, 518(1963); Astrophys. J. **141**, 364(1965).

[2] J. W. Cooper, U. Fano and F.Prats, Phys. Rev. Lett. **10**, 518 (1963).

[3] M. A. Hayes and M. P. Scott, J. Phys. B **21**, 1499 (1988); P. Hamacher and J. Hinze, J. Phys. B **22**, 3397 (1989); S. Salomonson, S. L. Carter, and H. P. Kelly, Phys. Rev. A **39**, 5111 (1989); R. Gersbacher and J. T. Broad, J. Phys. B **23**, 365 (1990); C. F. Fischer and M. Idrees, J. Phys. B **23**, 679 (1990); R. Moccia and P. Spizzo, Phys. Rev. A **43**, 2199 (1991); I. Sanchez and F. Martin, Phys. Rev. A **44**, 7318 (1991); T. N. Chang and X. Tang, Phys. Rev. A **44**, 232 (1991); D. H. Oza, Phys. Rev. A **33**, 824 (1986). R. Moccia and P. Spizzo, J. Phys. B **20**, 1423 (1987).

[4] J. Macek, J. Phys. B **1**, 831 (1968).

[5] C. D. Lin, Adv. At. Mol. Phys. **22**, 77 (1986).

[6] B. Christensen-Dalsgaard, Phys. Rev. A. **29**, 2242 (1984).

[7] C. D. Lin, Phys. Rev. A **23**, 1585 (1981).

[8] J. H. Macek, Phys. Rev. A **31**, 2162(1985).

[9] J. Z. Tang, S. Watanabe and M. Matsuzawa, Phys. Rev. A **46**, 2437 (1992).

[10] J. Z. Tang, S. Watanabe and M. Matsuzawa, Phys. Rev. A **46**, 3758 (1992).

[11] J. Z. Tang, S. Watanabe, M. Matsuzawa, and C. D. Lin, Phys. Rev. Lett. **49**, 1633 (1992).

[12] M. Domke, C. Xue, et al., Phys. Rev. Lett. **66**, 1306 (1991).