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## Simplified calculation of autoionization rates for doubly excited helium†

Donald L Miller‡ and Donald R Franceschetti§

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

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**Abstract.** KLL Auger transition rates for helium were computed using simple atomic orbital wavefunctions which take into account the difference in average electron-electron repulsion of initial and final states. The results are consistent with transition rates computed by other authors using a variety of many-electron techniques. It is suggested that wavefunctions determined in the manner described provide a useful approximate representation of the inner-shell region in the autoionizing state.

### 1. Introduction

The Auger effect, the decay of an atomic inner-shell vacancy state by autoionization, has been understood in principle for some time (Wentzel 1927). Although substantial literature concerning the phenomenon now exists (Bambynek *et al* 1972, Burhop and Asaad 1972), our understanding of autoionization in even the simplest atomic systems is far from complete. Recent developments in the field include the efforts of a number of authors (Propin 1960, Herrick 1973, Herrick and Sinanoğlu 1975, Sinanoğlu and Herrick 1975, Burke and McVicar 1965, Cooper *et al* 1967, Bhatia *et al* 1967, Bhatia and Temkin 1969, 1975, Bhatia 1972) to compute autoionization transition rates for doubly excited helium atoms, taking full account of the electron-electron interaction. The results of these calculations are significant for at least two reasons. (i) With only two electrons, the helium atom provides the simplest system available for the study of electron-electron correlation effects on any physical property. In view of the rapid increase in computational complexity with the number of electrons, it is quite likely that qualitative information gained from extensive calculations on helium will be applied to more complex systems before calculations of comparable accuracy are attempted. (ii) The existence of high-accuracy calculations for He permits the testing and refinement of simpler approximate methods more directly related to physical intuition. This paper reports the test of one such method. Although it neglects instantaneous electron-electron correlations, the method is shown to provide reasonable autoionization linewidths for helium. Its primary utility, however, derives from its direct applicability to the singly and multiply excited states

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‡ National Science Foundation Predoctoral Fellow.

§ Present address: Department of Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina 27514, USA.

of other low- $Z$  atoms and ions since most of these have not been studied by many-body methods.

Our approach employs an independent electron model in which wavefunctions are written as Slater determinants (or a simple linear combination thereof as required by symmetry) of atomic orbitals. Our method is based on the realization that the effective one-electron Hamiltonian (Fock operator (Fock 1930)), whose eigenfunctions provide the best single determinant approximation to the wavefunction of a given state, is unique to that state since it explicitly contains the averaged electron-electron repulsion of that particular state. Thus by determining initial- and final-state wavefunctions in independent calculations we are able to take into account the averaged electron-electron repulsion appropriate to each state.

We believe it useful to distinguish between this averaged repulsion, which might be obtained in an independent self-consistent single determinant calculation for each state, and the instantaneous correlation of electron motion which is included only in a full many-body treatment. Since some many-body methods (at least implicitly) expand all  $N$ -electron wavefunctions in terms of the same set of atomic orbitals, it may be difficult in such cases to differentiate between the two effects. The present calculation was undertaken in part to permit such a separation in the case of helium autoionization.

Earlier and more rudimentary calculations (Franceschetti 1974, Franceschetti and Dow 1974) have shown that in three-electron atoms the type of effect discussed here is an important factor in determining the rate of autoionization. The results presented here permit us to gauge the reliability of such calculations and provide guidance in approaching autoionization in other few-electron systems.

## 2. Method

The Auger transition rate is given in atomic units (energy unit = 2 Ryd) by the well known 'golden rule' formula

$$W = 2\pi |\langle f | (1/r_{12}) | i \rangle|^2 \rho_f(E). \quad (1)$$

The initial state  $|i\rangle$  involves an empty  $1s$  shell and the final state  $|f\rangle$  includes a continuum electron. We have determined initial- and final-state wavefunctions for all possible KLL Auger transitions by independent variational calculations.

The final-state wavefunctions were taken to be of the form

$$|f\rangle = \frac{1}{2}(\phi(1)\chi(2) \pm \chi(1)\phi(2))(\alpha(1)\beta(2) \mp \beta(1)\alpha(2)) \quad (2)$$

with signs chosen appropriately for singlet and triplet states.  $\phi$  was taken to be a hydrogenic  $1s$  function, as appropriate for the residual  $\text{He}^+$  ion, while the continuum function was determined by solving (Morse and Allis 1933)

$$(H_0 - \frac{1}{2}k^2 + J \pm K)\chi = \mp \langle \phi | H_0 - \frac{1}{2}k^2 | \chi \rangle \phi \quad (3)$$

where

$$H_0 = \frac{-\nabla^2}{2} - \frac{Z}{r} \quad (4)$$

is the hydrogenic Hamiltonian and  $\frac{1}{2}k^2$  is the energy of the continuum electron:

$$J\chi(r_1) = \left( \int d^3r_2 |\phi(r_2)|^2 r_{12}^{-1} \right) \chi(r_1) \quad (5)$$

and

$$K\chi(r_1) = \left( \int d^3r_2 \phi^*(r_2) \chi(r_2) r_{12}^{-1} \right) \phi(r_1) \quad (6)$$

define the direct and exchange Coulomb operators.

An iterative series of Numerov integrations was performed to provide self-consistent, numerical solutions of equation (3).

As mentioned above, the initial states were taken to be Slater determinants, or a linear combination thereof, as required in the *LS* coupling scheme. The independent electron orbitals used were of the form

$$\psi_{2s} = N_{2s} [r \exp(-\zeta_1 r) - \lambda \exp(-\zeta_2 r)] Y_{0,0}(\theta, \phi) \quad (7a)$$

$$\psi_{2p} = N_{2p} r \exp(-\zeta_3 r) Y_{1,m}(\theta, \phi) \quad (7b)$$

with  $\zeta_1, \zeta_2, \zeta_3$  being the variational parameters (Morse *et al* 1935). A separate variational calculation was performed for each *LS* term. In addition, configuration mixing of the  $2s^2$  and  $2p^2\ ^1S$  states was determined by diagonalization of the Coulomb operator. In calculations involving  $2s$  orbitals, the parameter  $\lambda$  was constrained to maintain orthogonality to the final-state  $1s$  orbital. This procedure provides physically reasonable wavefunctions with the assurance that the autoionizing states are approximately orthogonal to all lower lying states.

It should be noted that our method falls within the framework of Feshbach's 'Q-operator' formalism (Feshbach 1958, 1962, Geltman 1969). Within this framework, our autoionization widths are an approximation to the true value. Our energies, however, should be viewed as approximations to the eigenvalues  $\epsilon_\lambda$  of the operator  $QHQ$ , where

$$Q = (1 - |\phi(1)\rangle\langle\phi(1)|)(1 - |\phi(2)\rangle\langle\phi(2)|). \quad (8)$$

These eigenvalues differ from the true positions  $E_\lambda$  by an amount  $\Delta_\lambda$  which has been shown by other authors to be small (Bhatia and Temkin 1975).

### 3. Discussion

Table 1 includes the results of a number of recent calculations: Propin's (1960) four-term CI with screened hydrogenic wavefunctions, Herrick's (Herrick 1973, Herrick and Sinanoğlu 1975, Sinanoğlu and Herrick 1975) CI calculation using a much larger, but unscreened, hydrogenic basis, the close-coupling scattering theoretical calculations of Burke *et al* (Burke and McVicar 1965, Cooper *et al* 1967) and the calculation of Bhatia and Temkin, who employed a Hylleraas-type variational function within the projection-operator formalism (Bhatia 1972, Bhatia and Temkin 1969, 1975, Bhatia *et al* 1967). The latter provides the closest agreement with experiment (Berry *et al* 1972, Burrow 1970, Hicks and Comer 1975, Madden and Codling 1965, Rudd 1965) achieved to date, owing in part to the explicit appearance of  $r_{12}$  in the trial

**Table 1.** Energies (above ground state) and autoionization widths for doubly excited states of helium.

Energy (eV)					
$2s^2\ ^1S$	$2s2p\ ^3P$	$2s2p\ ^1P$	$2p^2\ ^1S$	$2p^2\ ^1D$	Source
59.42	58.49	61.10	62.31	60.93	This calculation (one configuration)
57.90	—	—	63.83	—	This calculation (two-term CI)
57.99	58.44	60.37	62.75	60.19	Propin (1960)
57.92	58.39	60.33	62.78	60.09	Herrick <sup>a</sup>
57.86	58.36	60.27	62.81	60.02	Burke <i>et al</i> <sup>b</sup>
57.84	58.32	60.15	62.09	59.91	Bhatia <i>et al</i> <sup>c</sup>
57.82 <sup>d</sup>	58.34 <sup>d</sup>	60.12 <sup>e</sup>	62.15 <sup>d</sup>	59.95 <sup>f</sup>	Experiment

  

Autoionization width (eV)					
$2s^2\ ^1S$	$2s2p\ ^3P$	$2s2p\ ^1P$	$2p^2\ ^1S$	$2p^2\ ^1D$	Source
0.091	0.018	0.032	0.049	0.105	This calculation (one configuration)
0.149	—	—	0.00095	—	This calculation (two-term CI)
0.221	0.033	0.024	0.004	0.087	Propin (1960)
0.14	0.022	0.036	0.0077	0.082	Herrick <sup>a</sup>
0.14	0.011	0.044	0.019	0.073	Burke <i>et al</i> <sup>b</sup>
0.125	0.0089	0.036	0.0067	0.073	Bhatia <i>et al</i> <sup>c</sup>
$0.138 \pm 0.015^g$	$0.0094 \pm 0.0006^h$	$0.038 \pm 0.004^e$	—	$0.072 \pm 0.018^g$	Experiment

<sup>a</sup> Herrick (1973), Herrick and Sinanoğlu (1975), Sinanoğlu and Herrick (1975).<sup>b</sup> Burke and McVicar (1965), Cooper *et al* (1967).<sup>c</sup> Bhatia (1972), Bhatia and Temkin (1969, 1975), Bhatia *et al* (1967).<sup>d</sup> Rudd (1965).<sup>e</sup> Madden and Codling (1965).<sup>f</sup> Burrow (1970).<sup>g</sup> Hicks and Comer (1975).<sup>h</sup> Berry *et al* (1972).

function, which allows a particularly accurate approximation to electron-electron correlation.

Examining the calculated energies, we find that our results, including  $2s^2$ – $2p^2$  configuration interaction, agree with the experimental values within 2%. All the other theoretical calculations included, however, achieve somewhat better agreement with experiment. It is often stated that the autoionization width is quite sensitive to the detailed nature of the atomic wavefunction (Bambynek *et al* 1972). A striking confirmation of this statement is found on comparing the results of Herrick (1973) and Propin (1960). Although the initial-state energies obtained by the two authors agree within 0.2% and their final-state wavefunctions are of the same form, their calculated linewidths disagree by as much as 50%. Our autoionization widths are in considerably better agreement with the results of the most detailed calculations (Bhatia 1972, Bhatia and Temkin 1969, 1975, Bhatia *et al* 1967) than those of Propin (1960) and agree nearly as well as those of Herrick (1973). The only disappointing result of our calculation is the very small width for the  $2p^2\ ^1S$  state. The Auger matrix element in this case involves the difference of nearly equal quantities and thus is extremely sensitive

to small inaccuracies in the atomic wavefunctions. It should also be noted that there is little agreement among previous calculations of this width.

The agreement observed between our calculated Auger widths and those obtained in far more detailed calculations leads us to believe that the essential physical factors determining the Auger transition rate are well represented in our wavefunctions. This is at first surprising since our independent electron wavefunctions, obtained in simple variational calculations, are not even self-consistent solutions of the Hartree–Fock equations. We argue, however, that (i) the self-consistent solution of the Hartree–Fock equation is a particularly good approximation to the true wavefunction for most of the doubly excited states considered, (ii) our variational calculations produce wavefunctions which closely approximate the self-consistent wavefunctions in the inner-shell region and (iii) the behaviour of the wavefunction in the inner-shell region is the most important factor determining the Auger transition rate.

The dominant contribution to the energy of a doubly excited state is the electron–nucleus attraction. (Note that this contribution is proportional to  $\langle r^{-1} \rangle$  while the electron–electron repulsion contribution is roughly proportional to  $1/\langle r^2 \rangle$ .) Starting with the best independent electron approximation to the  $2l' \ 2s+1L$  state, one expects only small configuration interaction admixtures of higher  $nl''n'l''' \ 2s+1L$  states ( $n$  or  $n' > 2$ ) since those admixtures reduce electron–electron repulsion only at the cost of increasing the electron–nucleus separation. For the transitions considered here, one therefore need only be concerned with the interaction of the  $2s^2$  and  $2p^2 \ 1S$  states, since those states correspond to nearly equal values of  $\langle r^{-1} \rangle$  and their interaction permits electron correlation without increasing the electron–nucleus separation.

The largest contribution to  $\langle r^{-1} \rangle$  arises from the region of the atom within the first Bohr radius. Since  $\langle r^{-1} \rangle$  determines the greater part of the total energy, a variational calculation will provide a good approximation to the wavefunction in that region, even at the expense of an accurate description of the wavefunction in other regions, provided that the trial function provides sufficient flexibility. We note that a trial function with variable exponents (equation (7)) is particularly suitable in this respect.

Cooper (1964) and Fano and Cooper (1965) have pointed out that despite the long-range nature of the Coulomb interaction, the dominant contribution to the Auger matrix element

$$\int d^3r_1 \int d^3r_2 \psi_f^*(r_1, r_2) \frac{1}{r_{12}} \psi_i(r_1, r_2) \quad (9)$$

arises from the region in which both electrons are near the nucleus. Since  $\psi_f$  involves a  $1s$  electron, the dominant contribution to this matrix element arises from the region of configuration space in which both electrons are near the nucleus, for in that region both  $\psi_f$  and  $r_{12}^{-1}$  will be large. Thus the initial-state wavefunctions employed in our calculation, although simple in form, permit a close approximation to the actual transition rate.

#### 4. Summary

We have presented a simple method for the calculation of KLL Auger transition rates of low- $Z$  atoms and ions. Wavefunctions employed are single Slater determinants (or simple linear combinations) and initial and final states are determined

in independent variational calculations. The method is based on the realization that the average electron-electron repulsion may differ considerably in initial and final states.

KLL decay rates were computed for doubly excited helium and compared with the results of experiment and high-accuracy calculations. The results suggest that the autoionization width may be reliably estimated without taking into account the instantaneous correlation of electron motion. It is reasonable to expect that similar physical considerations govern the decay of single and double K-shell vacancies in other low- $Z$  atoms. Calculations of the autoionization width in such systems using the method described should distinguish between long-lived and short-lived states and should predict the width of the latter to within a factor of two.

It is only a matter of time before high-accuracy configuration-interaction calculations are available for the autoionization of atoms with more than two electrons. We feel, however, that simple, physically inspired methods will remain valuable both in sorting out experimental data and in advancing our conceptual understanding of the autoionization process.

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