CALCULATION OF AUTOIONIZATION STATES OF He AND H⁺

Albert P. HICKMAN, Alan D. ISAACSON and William H. MILLER

Department of Chemistry, and Inorganic Materials Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA

Received 10 July 1975

The positions and lifetimes of several 1S and 1P autoionizing states of He and H⁺ are obtained by two methods involving standard techniques of electronic structure calculation which can be extended to more complicated systems. The first method involves an approximate evaluation of Miller's "golden rule" formula; the second is an application of the recently developed complex coordinate method.

1. Introduction

Recent calculations [1,2] of the autoionizing states of two-electron systems have been carried out to a very high degree of accuracy. However, these calculations utilize Hylleraas basis sets and other techniques which cannot easily be extended to more complicated systems. We have performed calculations of the positions and lifetimes of several autoionizing states of He and H⁺ by two methods involving standard techniques of electronic structure calculation. The first method is a direct extension of the stabilization method [3] and involves an approximate evaluation of Miller's [4] golden rule formula. The second method is an application of the recently-developed complex coordinate approach [2,5], in which the coordinate operators $r_j$ in the hamiltonian are replaced by $e^{i k r_j}$, and matrix elements are evaluated in an appropriate basis set. The complex eigenvalues $E_r - \frac{1}{2} i \Gamma$ of this matrix give directly the position and width of autoionizing states. We have obtained results accurate to about ten percent using Slater-type basis sets of modest size. Both of these methods may be extended to molecular systems, and thus may prove useful in the calculation of electron-molecule scattering resonances and widths for Penning ionization.

2. Golden rule calculations

The familiar golden rule of Miller [4] is given by

$$\Gamma = 2 \pi \rho (\psi_r | H - E_r | \chi_c)^2.$$  

$\psi_r$ is the resonance electronic wavefunction corresponding (for example) to a doubly excited state of He, $\chi_c$ is then a continuum wavefunction of the system He⁺ + e⁻. $\rho$ is the density of continuum states.

Our approach is to approximate $\chi_c$ by one of the non-resonance eigenfunctions of the hamiltonian matrix constructed by the CI procedure. That is, we begin with a basis set of $N$ orthonormal configurations $\{ \Phi_i(r_1, r_2) \}$, and diagonalize the matrix $H_{ii} = \langle \Phi_i | H | \Phi_i \rangle$. As in the standard stabilization procedure, we identify one root as the resonance:

$$\psi_r = \sum_{i=1}^{N} a_{ri} \Phi_i.$$  

It has been found [3] that some of the other $N-1$ eigenfunctions of $H_{ii}$ correspond to "continuum-like" solutions of $H_i$, i.e., to He⁺ + e⁻:

$$\tilde{\chi}_c = \sum_{i=1}^{N} a_{ci} \Phi_i.$$
Table 1

<table>
<thead>
<tr>
<th>Basis sets for golden rule calculations</th>
<th>(3P)</th>
<th>(1P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>(Z = 2.00)</td>
<td>(Z = 2.00)</td>
</tr>
<tr>
<td>2s</td>
<td>0.74</td>
<td>0.56</td>
</tr>
<tr>
<td>2p</td>
<td>0.85</td>
<td>0.99</td>
</tr>
<tr>
<td>(2p', 3p-8p)</td>
<td>1.71–1.81</td>
<td>1.71–1.81</td>
</tr>
</tbody>
</table>

Before substituting into the golden rule formula, it is necessary to "project out" from \(\psi_\tau\) all configurations which correspond to continuum-like solutions; otherwise the orthonormality of the eigenfunctions \(\psi_\tau\) and \(\chi_c\) would yield a zero result. It is then easily shown that

\[
\Gamma = 2\pi \rho(E_\tau - E_c)^2 \sum |a_{\tau i}a_{c i}|^2,
\]

where the prime on the summation emphasizes that certain configurations are not included.

Calculations were performed on the \(2s2p\) \(3P\) states of He using the basis sets shown in table 1. Several diffuse basis functions have been included to represent the continuum orbital. Typically we used nine configurations: 1s2p, 2s2p, 1s2p', 1s3p, ..., 1s8p (where each STO has been orthogonalized to those preceding it in table 1). Initially it was hoped that the roots would correspond to the resonance state closely bracketed by continuum-like solutions. The continuum roots, however, proved not to be so closely spaced. We therefore decided to adjust the \(Z\) of the \(2p'-8p\) basis functions in order to have one continuum solution very close to the resonance solution. This was effective. As \(Z\) was varied, the energy of the continuum root closest to resonance moved continuously through an interval about \(E_\tau\). Eq. (4) breaks down and gives zero if \(E_c = E_\tau\), so we determined \(\Gamma\) for several values of \(Z\) which gave \(E_c\) close to \(E_\tau\) and interpolated. The value of \(E_\tau\) was relatively stable against variation in \(Z\). As previously stated, all continuum-like configurations 1s2p', 1s3p, ..., 1s8p are excluded from the sum. \(\Gamma\) is thus a direct measure of the amount of the resonance \(2s2p\) configuration in the continuum state, or, alternatively, of the amount of continuum configurations in the resonance states.

We determined the density of continuum states \(\rho\) by using a result discussed previously by Hazi and Taylor [3]. They found that the use of square integrable functions which form a flexible basis out to some large distance \(L\), but which then decay rapidly, corresponds approximately to the boundary condition of an infinite potential barrier at \(L\). The energies of the continuum states of He\(^+\) + e\(^-\) should then be approximately \(E_n = -\frac{1}{2}Z^2 + \frac{1}{2}k_n^2\), where \(-\frac{1}{2}Z^2\) is the energy of the He\(^+\) core, and

\[
k_n \approx 2\pi n/L.
\]

If the integral of \(\psi^*\psi\) is normalized to unity (as is done automatically in our CI calculations), then \(\rho(E_n)\) is given by

\[
\rho = (\frac{1}{2}k_n^2)^{-1} - (\frac{1}{2}k_{n-1/2}^2)^{-1}.
\]

\(k_n\) was determined for each continuum eigenvalue, and found to be very nearly linear in \(n\) near the resonance. We were therefore able to determine \(\rho\) with an accuracy of 10–15%. Fig. 1 shows our results for He(2s2p \(3P\)); the value obtained for \(\Gamma\) agrees quite well with the accurate values of Bhatia and Temkin [1]. For He(2s2p \(1P\)) the method gave \(\Gamma\) about a factor of two too small. These results are summarized in table 2.

3. Complex coordinate method

A more direct approach for calculating the energies of autoionizing states is the recently developed complex coordinate method [2,5]. In this approach all the radial coordinates in the Hamiltonian are considered to be complex \((r \rightarrow e^{ikr})\), and the resulting Schrödinger equation is

\[
\left[ -\frac{1}{2}e^{-2ik}(\nabla_1^2 + \nabla_2^2) - \frac{Ze^{-ik}}{r_1} - \frac{Ze^{-ik}}{r_2} + \frac{e^{-ik}}{r_{12}} - E \right] \psi = 0.
\]
Table 2
Summary of results

<table>
<thead>
<tr>
<th>State</th>
<th>Golden rule method</th>
<th>Complex coordinate method</th>
<th>Accurate values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_f$(au)</td>
<td>$\Gamma$(eV)</td>
<td>$E_f$(au)</td>
</tr>
<tr>
<td>He</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^1S$</td>
<td>-0.6577</td>
<td>0.021</td>
<td>-0.7767</td>
</tr>
<tr>
<td>$^1P$</td>
<td></td>
<td></td>
<td>-0.6618</td>
</tr>
<tr>
<td>$^3P$</td>
<td>-0.7504</td>
<td>0.0085</td>
<td>-0.7552</td>
</tr>
<tr>
<td>H$^-$</td>
<td></td>
<td></td>
<td>-0.1484</td>
</tr>
<tr>
<td>$^1S$</td>
<td></td>
<td></td>
<td>-0.1382</td>
</tr>
</tbody>
</table>

\[a\] Results for this state are also obtained in refs. [2,5].

It has been shown [6] that the bound state eigenvalues $E$ of this transformed equation are independent of $\alpha$, and that the continuum solutions have energies along rays in the complex plane which make an angle $2\alpha$ with the real axis, and which intersect the real axis at each eigenenergy of the one electron system. The location of autoionizing states (which correspond to scattering resonances or poles of the $S$ matrix) is also independent of $\alpha$; the wavefunctions for these states decay asymptotically for $\alpha$ in a certain range. Thus, after a coordinate rotation, autoionizing states and genuine bound states are both described by square integrable wavefunctions, and both may be calculated with the same techniques. Using modest but carefully selected basis sets of Slater orbitals, we have calculated the spectrum of eigenvalues of certain $^1S$ and $^1,^3P$ states of He and H$^-$, and found the behavior of the bound, autoionizing, and continuum states in accord with the prediction an exact calculation. Previous complex coordinate calculations [2,5] of two electron systems have dealt with the $^1S$ state of H$^-$. We typically chose basis sets of about 13 STO's, formed linear combinations of them to construct 4 to 60 configurations which were eigenfunctions of $M_L$, $S^2$, and $M_S$. As in the previous section, we chose several very diffuse basis functions, to allow the wavefunctions to have a flexible asymptotic form. Fig. 2 illustrates our results for the $^3P$ symmetry of H$^-$, $S$ were accurately obtained belonging to two different continua, $e^- + H(1s)$ and $e^- + H(2s)$. States were also found which seem to belong to the $e^- + H(3s)$ continuum, but they do not lie exactly on the ray as expected. This presumably reflects the limited nature of our basis.

Fig. 3 shows the trajectory of the energy of the...
2s2p $^3P$ autoionizing state of He. For $\alpha = 0$, this is just the energy obtained in a stabilization calculation. For $\alpha > 0$, the root should rapidly approach the exact pole location and remain there. Instead, we observe the same behavior as did Doolen et al. [2]; the root trajectories approach the exact pole locations, hesitate, and then move rapidly away. We calculated $\text{IdE/dal}$ along the trajectory, and defined our best estimate of the pole's location as the point where this quantity was a minimum. Thus in fig. 3 the root location is plotted for equal increments $\Delta \alpha = \pi/96$; a range of $\alpha$ exists over which both the real and imaginary parts of the energy are nearly stationary.

An explanation for this behavior is suggested by the results of calculations we carried out using the same model potential as Bain et al., viz., $V(r) = 7.5 \ r^2 e^{-4}$ au. For several $\alpha$, we calculated the complex wavefunctions numerically and compared them with those generated by the complex matrix diagonalization. For small $\alpha$, the basis set was flexible enough to reproduce accurately the real and imaginary parts of the wavefunction, and the resonance eigenvalue was stationary. However, as $\alpha$ was increased, the exact wavefunction exhibited additional oscillations which the basis set could not reproduce. At this point the trajectory followed by the resonance root moved away from the exact pole, in a seemingly random direction.

It is likely that the behavior of the resonance roots for the two electron system is also related to the adequacy of the basis set at each angle $\alpha$. We found the following expansion a useful guideline for choosing basis functions:

$$r\rho^m \exp(-Zre^{i\alpha}) = r^\mu (e^{-Zr \cos \alpha} - iZr \sin \alpha e^{-Z \cos \alpha} + ...). \quad (8)$$

Thus if an STO of order $n$ and charge $Z$ is important in describing a particular state for $\alpha = 0$, one might expect higher order STO's of charge $Zcos \alpha$ to be appropriate at the rotation angle $\alpha$. We normally included only one higher order function, and used double-zeta basis sets to span a range of Z's.

Table 2 summarizes the results of our calculations. We feel that of the two methods we have tried, the complex coordinate method is the more promising. This method yields lifetimes accurate to about ten percent for a variety of autoionization states, and requires very little effort beyond that for a standard, real, bound state calculation. Undoubtedly, this accuracy could be improved by the use of more elaborate basis sets. However, we are presently working to extend the method to molecular systems.

References