

## Use of a diabatic molecular expansion in studies on electron capture by $\text{He}^{2+}$ ions in helium at keV energies

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**Abstract.** In this preliminary work, using a 3-state diabatic molecular expansion without any excited channels, we have studied within the semiclassical impact parameter approximation the single charge transfer process  $\text{He}^{2+} + \text{He}(1s^2) \rightarrow \text{He}^+(1s) + \text{He}^+(1s)$ . Our results agree very well with experiment, which demonstrates the usefulness of this type of diabatic molecular basis in doubly charged ion-atom collision systems.

**Keywords.** Diabatic molecular expansion; ion-atom collision.

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In ion-atom collisions at low energies, a quasimolecular description of the collision complex is appropriate, and there have been many attempts (e.g. [1–8]) to define diabatic molecular states, although no unique definition still exists. We have recently initiated a programme of studying low-energy charge transfer collisions between atoms and doubly charged ions, using diabatic molecular wavefunctions constructed somewhat similarly as in an earlier work [9] devoted to  $\text{He}^+ - \text{He}$  collisions. Before embarking on large-scale calculations, we decided to try out a simple 3-configuration basis on the  $\text{He}^{2+} - \text{He}$  single charge transfer problem for which extensive data are available [10–12]. We found that this simple diabatic basis accounts extremely well for single charge transfer to the ground state [11] for the above system. We feel that this demonstrates the basic usefulness of this type of diabatic basis in collision problems, and we are now pursuing this approach with a larger, more state-of-the-art basis set including excited channels to study single as well as double charge transfer collisions; meanwhile, we report here our preliminary findings.

We are using atomic units throughout except where otherwise stated. Expand the total wavefunction of the collision complex in a truncated basis

$$\Psi(\mathbf{r}, \mathbf{R}(t)) = \sum_k c_k(t) \psi_k(\mathbf{r}, \mathbf{R}). \quad (1)$$

Then in the semiclassical impact parameter approximation, the time-dependent Schrödinger equation becomes (see [9] for details)

$$i \frac{dc_j}{dt} = \sum_k (H_{jk} + P_{jk} + Q_{jk}) c_k \quad (2)$$

where

$$H_{jk} = \langle \psi_j | H_{e1} | \psi_k \rangle,$$

$$P_{jk} = \frac{vz}{R} \left\langle \psi_j \left| -i \frac{\partial}{\partial R} \right| \psi_k \right\rangle,$$

$$Q_{jk} = \frac{vb}{R^2} \left\langle \psi_j \left| -i \frac{\partial}{\partial \theta} \right| \psi_k \right\rangle$$

where  $z = vt$ , and  $b$  is the impact parameter. (There is an obvious misprint in the last line of eq. (7) in [9].)

For use in (1-2) we now define a diabatic molecular basis as in [9]:

$$\psi(\mathbf{r}, R) = \mathbf{U}(R = \infty) \mathbf{S}(R) \phi(\mathbf{r}, \xi(R = \infty); R) \quad (3)$$

where  $\psi$  and  $\phi$  are column vectors,  $\xi$ 's are the orbital exponents,  $\mathbf{S}(R)$  is the Schmidt orthonormalization matrix and  $\mathbf{U}$  diagonalizes  $\langle \mathbf{S} \phi | H_{e1} | \mathbf{S} \phi \rangle$  at large  $R$ . The centre of mass coincides with the centre of charge for a symmetric system, and has been chosen as the origin of coordinates. Obviously, at large  $R$ ,  $\psi$  coincides with the adiabatic basis. We are concerned with the low-energy region ( $v < 1$  a.u.), and for the present choose to omit the electron translation factors (ETF's).

In this work concentrating on electron capture into the ground state only, we choose a three-state expansion as follows (apart from normalization factors):

$$\phi_1 = 1\sigma_g^2 + 1\sigma_u^2 \quad ({}^1\Sigma_g),$$

$$\phi_2 = 1\sigma_g^2 - 1\sigma_u^2 \quad ({}^1\Sigma_g),$$

$$\phi_3 = |1\sigma_g 1\bar{\sigma}_u| + |1\sigma_u 1\bar{\sigma}_g| \quad ({}^1\Sigma_u)$$

where the molecular orbitals  $1\sigma_{g,u} = \frac{1}{\sqrt{2}}[1s(A) \pm 1s(B)]$ . Minimal (single-zeta)

Slater-type functions were used as the atomic orbitals, the exponents being chosen to obtain variational minima of the eigenvalues at large  $R$ . Table 1 lists the exponents at  $R = 50$  a.u., together with the energy values. Note that the  $\phi$ 's have gone over to the correct separated-atom energies [13].

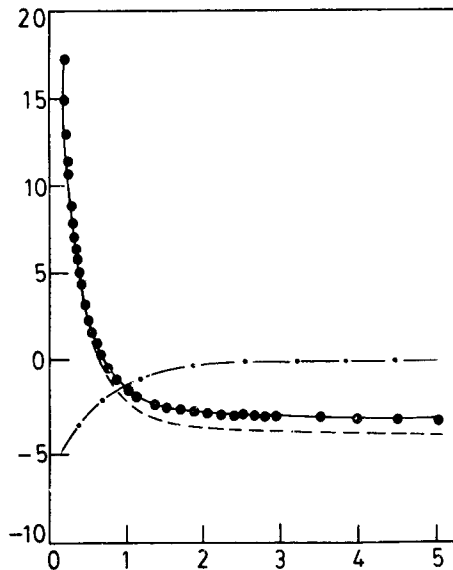
We now freeze the exponents and the  $\mathbf{U}$  matrix at  $R = 50$  a.u. to form the diabatic basis (3) extending over all  $R$ . As shown in [9], this basis is a close approximation to the standard radial diabatic representation defined by Smith [3] in that  $\mathbf{P}$  is negligible throughout; also, since (3) involves  $\Sigma$ -states only, the rotational coupling

**Table 1.** Basis functions used to construct the diabatic molecular wavefunctions (3).

Basis function	Separated atom limit	Atomic orbital exponent	Energy (a.u) at $R = 50$ a.u
$\phi_1, \phi_3$	$\text{He}_A(1s^2) \pm \text{He}_B^+ +$	1.6875	- 2.847656*
$\phi_2$	$\text{He}_A^+(1s) + \text{He}_B^+(1s)$	2.00	- 3.980000

\*Agrees exactly with the single-zeta energy for He (e.g. Clementi and Roetti [13]).

### Diabatic molecular expansion



**Figure 1.** Diabatic Hamiltonian matrix elements for the basis (3) of text plotted against internuclear distance. Full-line curve,  $H_{11}$ ; dots,  $H_{33}$ ; dashed curve,  $H_{22}$ ; dot-dashed curve,  $H_{12}$ .

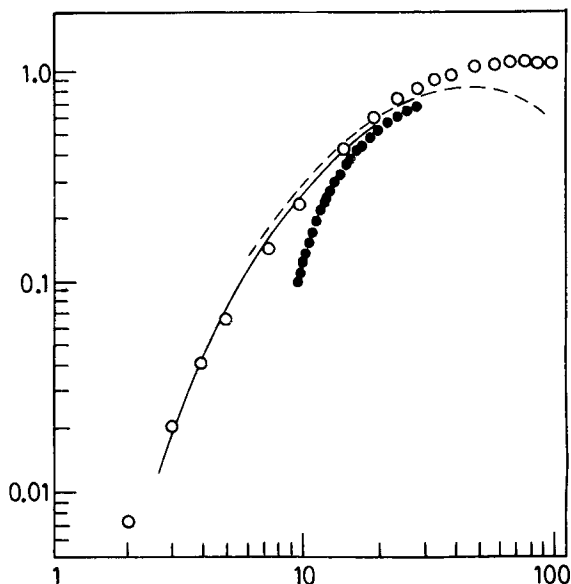
matrix  $\mathbf{Q}$  is identically zero. The coupled equations (2) now involve  $\mathbf{H}$ -matrix elements only. One of the equations is uncoupled with the others and is trivially solved, and we solved the other two coupled equations by a variable-step fourth-order Runge-Kutta method which preserved unitarity to within 1 part in  $10^4$ . The cross-sections for the charge transfer reaction



were then obtained by standard methods. Details of numerical procedures can be found elsewhere [14].

Figure 1 shows the frozen-orbital diabatic energies and the coupling term  $H_{12}$ . As table 1 shows, the diagonal terms go over to the correct separated-atom values. The off-diagonal coupling  $H_{12}$  decays exponentially, and from the figure it is obvious that we have a Demkov-type coupling here between the states  $\psi_1$  and  $\psi_2$ . Space limitations do not permit displaying our results for the charge transfer probabilities; we found, however, that their velocity dependence follows the pattern predicted by Demkov [15].

Figure 2 shows our results for the total cross-section of the single capture process (4) as a function of collision energy. The results shown above 25 keV/amu ( $v \sim 1$  a.u.) may be deemed simply an extrapolation of our code into the so-called “intermediate-energy region”, and not really a “prediction” of our low-energy theory. Also displayed are the experimental results of Afrosimov *et al* [11] and the theoretical results of Fulton and Mittleman [16] and of Gramlich *et al* [21]. Although the  $\text{He}^+ - \text{He}$  collision has been theoretically treated by several groups [16–22], total cross-sections for the process (4) have been given only by three groups [16, 18, 21]. Fulton and Mittleman [16] used a three-state atomic orbital expansion; Harel and Salin [18] used a twelvestate adiabatic molecular expansion built with one-electron diatomic



**Figure 2.** Single charge transfer cross-section for reaction (4) ( $10^{-16} \text{ cm}^2$ ) plotted against collision energy (keV/amu). Open circles, present results (see text); full-line curve, data of Afrosimov *et al* [11]; dashed curve, calculations of Fulton and Mittleman [16]; full circles, calculations of Gramlich *et al* [21].

molecular orbitals, while Gramlich *et al* [21] used a Gaussian atomic orbital expansion. ETF's were included in [16] and [21] but not in [18]. Comparison of our results with these experimental and theoretical works in figure 2 reveals the following features:

- (1) Our results agree very well with the data of Afrosimov *et al* [11]. Although this is in accord with the observation of Zygelman *et al* [23] that a molecular-state expansion without electron translation factors is a valid low-energy approximation for charge transfer processes, we prefer to try out a larger basis before arriving at any conclusion on this point, inasmuch as this is linked with the question of origin-dependence of the results.
- (2) The results of Fulton and Mittleman [16] and of Harel and Salin [18] (not shown) compare with experiment almost equally well as ours. Harel and Salin find, however, that leaving out excited-channel configurations (basis  $\phi_3^g$ ,  $\phi_6^g$  and  $\phi_4^u$  in their paper) yields theoretical results much lower than experiment, and from this they conclude that the ground level is populated principally through a complicated mechanism. Our results agree well enough with experiment to indicate that in the low energy regime, use of diabatic molecular expansions seems to allow us to ignore the excited channels, whereas use of adiabatic expansions does not. (The situation appears somewhat similar to Lichten's first use [1] of diabatic states in  $\text{He}^+ - \text{He}$  collisions.) We, however, reserve our final judgement on this point till we try out a larger basis with excited channels. The results of Gramlich *et al* [21] do not compare well with our results in the energy range shown; however, their basis set was of a nature different from ours, and not much can be gained from this comparison. We note that Gramlich *et al* did not discuss the specific point above regarding the importance of the excited channels for the reaction (4).

### Diabatic molecular expansion

Summarizing, we have demonstrated the usefulness of a very simple diabatic molecular basis in a doubly charged ion-atom collision system at low energies. Work is in progress to study charge transfer channels into excited states and also to check on what may be called the size-consistency of this basis set for the problem of charge transfer into the ground state.

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