Resonant charge transfer in slow Li^+–Li(2s) collisions*

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The resonant charge transfer process for Li^+–Li(2s) collision is investigated by the quantum-mechanical molecular orbital close-coupling (QMOCC) method and the two-center atomic-orbital close-coupling (AOCC) method in an energy range of 1.0 eV/u–10^4 eV/u. Accurate molecular structure data and charge transfer cross sections are given. Both the all-electron model (AEM) and one-electron model (OEM) are used in the QMOCC calculations, and the discrepancies between the two models are analyzed. The OEM calculation can also give a reliable prediction of the cross sections for energies below 1 keV/u.

Keywords: resonant charge transfer, Li^+–Li(2s) collisions, cross section

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1. Introduction

For the homonuclear collision process like $Li^+ + Li \rightarrow Li + Li^+$, the charge transfer is much more important than the elastic process, and so it is called the resonant charge transfer process. The resonant charge transfer between alkali-ion and alkali-atom collisions has received considerable attention both experimentally and theoretically. The extraordinarily large cross sections at low collision energies make it important in a number of applications such as ion propulsion and ionization in high-temperature gases.[1] As a quasi-one-electron homonuclear collision system, the Li^+–Li(2s) collision system has been investigated extensively both experimentally and theoretically.[1–7] In particular, wide-spread theoretical interest was attracted by the oscillation structures shown in the total charge-transfer cross sections observed by experimental researchers. The first theoretical investigation of this system was made by Peek *et al.*[4] by using a two-state expansion approach. The oscillations in the cross sections were predicted. McMillan[5] calculated the charge transfer cross sections for resonant and nonresonant processes by using a three-state molecular orbital close-coupled (MOCC) method. Allan and Hanssen[6] and Men *et al.*[7] also investigated the charge transfer processes of Li^+–Li(2s) collisions with a similar MOCC method. However, controversies still remain in the resonant charge transfer cross sections at the low-energy region (below 20 eV/u) and high-energy region (above 1 keV/u). As far as we know, except the work of Allan and Hanssen,[6] in which a 12-state approximation was employed, other available theoretical calculations are all based on a two-state or three-state approximation. All of these theoretical studies are performed within the framework of the one-electron model (OEM) and the motion of the nuclei is treated classically (SMOCC). In the low-energy region, the impact parameter method is invalid and a fully quantum-mechanical treatment should be employed. At high energies, the cross sections sensitively depend on the accuracy of the molecular data at small internuclear distances. It is essential to use the accurate molecular data with an all-electron model (AEM); by considering the complex state couplings at small distances, more states should be involved in the MOCC calculation.

In order to investigate the influence of the core electrons and to obtain accurate cross sections of Li^+–Li(2s) collisions in a wide energy region, we undertake a thorough *ab initio* theoretical treatment for the resonant charge transfer reaction of Li^+–Li(2s) collisions within the framework of OEM and AEM. The quantum-mechanical MOCC (QMOCC)[8,9] calculation is performed with the electron translation factors (ETFs) included at energies of 1-5000 eV/u. An *ab initio* multireference single- and double-excitation configuration interaction (MRD-CI) package[10,11] is utilized to calculate the molecular data (potential curves, radial and rotational coupling matrix elements) required in the QMOCC calculation. The two-center atomic orbital close coupling (AOCC) method[8,12] is also employed in an intermediate energy range of 0.1 keV/u–10 keV/u.

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2. Theoretical method

2.1. QMOCC method

In this section we only present the basic technique of the QMOCC method for the present collision system. A more detailed account of the description can be found in Refs. [8] and [9]. In the QMOCC method, a coupled set of second-order differential equations was solved by the log-derivative method.[13] The radial and rotational (A^r and A^θ) couplings are responsible for driving the transition between channels. Considering the interchange of the two identical nuclei, the electron wave function has gerade (g) and ungerade (u) manifolds. The coupled sets of differential equations are solved separately for the g- and u-states and matched to the plane-wave boundary conditions. By the obtained $S^{\mathrm{g,u}}$ matrices, the scattering amplitudes of the g- and u-channels can be expressed as the following standard form:[8]

$$f_{ij}^{\mathrm{g,u}}(E,\theta)=\frac{1}{2\mathrm{i}k_i}\sum_{J=0}^{\infty}(2J+1)\left(S_{ij,J}^{\mathrm{g,u}}-\delta_{ij}\right)\mathrm{P}_J(\cos\theta), \quad (1)$$

where k_i denotes the initial momentum for center-of-mass motion, J is the total angular momentum quantum number, and P_J is the Legendre polynomial of order J.

The cross sections are given for direct scattering and charge transfer by the following expressions:

$$\begin{aligned}\sigma_{i\to j}^{\mathrm{d}}&=\frac{\pi}{k_i^2}\sum_{J=0}^{\infty}(2J+1)\left|\left(S_{ij,J}^{\mathrm{d}}-\delta_{ij}\right)\right|^2,\\ \sigma_{i\to j}^{\mathrm{ex}}&=\frac{\pi}{k_i^2}\sum_{J=0}^{\infty}(2J+1)\left|\left(S_{ij,J}^{ex}-\delta_{ij}\right)\right|^2,\end{aligned} \quad (2)$$

respectively, where the S matrices are given by

$$\begin{aligned}S_{ij,J}^{\mathrm{d}}(E,\theta)&=\frac{1}{2}\left[S_{ij,J}^{\mathrm{g}}+S_{ij,J}^{\mathrm{u}}\right],\\ S_{ij,J}^{\mathrm{ex}}(E,\theta)&=\frac{1}{2}\left[S_{ij,J}^{\mathrm{g}}-S_{ij,J}^{\mathrm{u}}\right],\end{aligned} \quad (3)$$

corresponding to the direct scattering and charge transfer processes.

2.2. AOCC method

The details of the two-center AOCC methods can be found in the literature,[8,12] which we shall only outline briefly. The total electron wavefunction is expanded in terms of bound atomic orbitals of the two ionic centers, (ϕ^A, ϕ^{B}), multiplied by plane wave ETFs,

$$\Psi(\boldsymbol{r},t)=\sum_i a_i(t)\phi_i^A(\boldsymbol{r},t)+\sum_j b_j(t)\phi_j^B(\boldsymbol{r},t). \quad (4)$$

For the Li^+ ions, the frozen core approximation is employed. The interaction between the active electron and the ionic cores is expressed by model potential[5] (for Li^+ ions)

$$V_{\mathrm{Li}^+}(r)=-\frac{1}{r}-\frac{1}{r}(2+3.310r)\,\mathrm{e}^{-3.310r}. \quad (5)$$

Adopting the straight-line approximation for nuclear motion, and substituting the expansion (4) into the time-dependent Schrödinger equation, we can obtain the first-order coupled equations:

$$\begin{aligned}\mathrm{i}(\dot{A}+S\dot{B})&=HA+KB,\\ \mathrm{i}(\dot{B}+S^{\dagger}\dot{A})&=\bar{K}A+\bar{H}B,\end{aligned} \quad (6)$$

where A and B are the vectors of the amplitudes a_i and b_j, respectively; S is the overlap matrix ($S^{\dagger}$ is its transposed form); H, $\bar{H}$, and K, $\bar{K}$ are the direct and exchange coupling matrices.

By integrating corresponding translational probabilities over the impact parameter, the cross section for charge transfer can be obtained by

$$\sigma_j=2\pi\int_0^{\infty}|b_j(+\infty)|^2 b\,\mathrm{d}b. \quad (7)$$

In our AOCC calculations for the present collision system, the projectile basis includes all atomic states with $n\le 4$, while on the target all $n\le 3$ bound states are included in the basis.

3. Results and discussion

3.1. Molecular structures

For the molecular structure calculations of the Li^+–Li(2s) system, the potential produced by the core electrons and the Li atomic nuclei is usually replaced by the pseudopotential or model potential. In the present study, both the all-electron model (AEM) and one-electron model (OEM) are used in the *ab initio* MRDCI,[10,11] calculations for the potential energy curves of the five lowest $^2\Sigma_{\mathrm{g}}^+$, five $^2\Sigma_{\mathrm{u}}^+$, three $^2\Pi_{\mathrm{g}}$, and three $^2\Pi_{\mathrm{u}}$ electronic states of the Li_2^+ molecular ion. The subscripts g and u represent the asymmetric and anti-symmetric combinations of the electron wave functions for the exchange of the two lithium nuclei. In OEM, all the inner-shell electrons are frozen and only the valence electron (2s for Li) is considered in the *ab initio* self-consistent field (SCF) and CI calculations. For the Li atom, a (2s1p2d) diffuse set adding to the cc-pVTZ type basis set[14] are employed. The differences between the present calculated asymptotic energies and the experimental results[14] are less than 210 cm^{-1}. The radial and rotational couplings are then calculated with the obtained electronic wave functions by using the finite differential and analytical methods, respectively.[16] In this work, the translational effect was taken into account by introducing the common translation factors with the method of Bacchus–Montabonel.[17]

Potential energy curves of the Li_2^+ ion calculated with AEM and OEM are presented in Figs. 1(a) and 1(b), respectively, in the internuclear distances of $R=0.9$ a.u.–30 a.u. (the unit a.u. is the atomic unit). The $1^2\Sigma_{\mathrm{g}}^+$ and $1^2\Sigma_{\mathrm{u}}^+$ states, corresponding to [Li^+ + Li(2s)] and [Li(2s) + Li^+] asymptotic

($R = \infty$) configurations, represent the initial channels for the Li^+–Li(2s) collisions. At low collision energies, the collision process can be treated as a two-state problem because the $1^2\Sigma_g^+$ and $1^2\Sigma_u^+$ states do not couple with upper states. The resonant charge transfer would be the dominant inelastic process under these conditions. The translation probability is determined by the interference between the gerade and ungerade scattering amplitudes.[8]

In Table 1, we present the values of equilibrium distance R_e and the depth of potential well D_e of the present calculated states. Our results are also compared with the available theoretical calculations.[7,18–20] It can be observed that the present calculated spectroscopic constants with AEM and OEM are both reliable and agree well with each other for the ground state and the low-lying energy states. For the high-energy states such as $4^2\Sigma_g^+$, $4^2\Sigma_u^+$, and $2^2\Pi_g$, some discrepancies can be found between the results acquired from the two models. However, such discrepancies would have a limited influence on the dynamics calculations, since the resonant charge transfer between $1^2\Sigma_g^+$ and $1^2\Sigma_u^+$ is the dominant process in the collision system for the considered collision energies in this work.

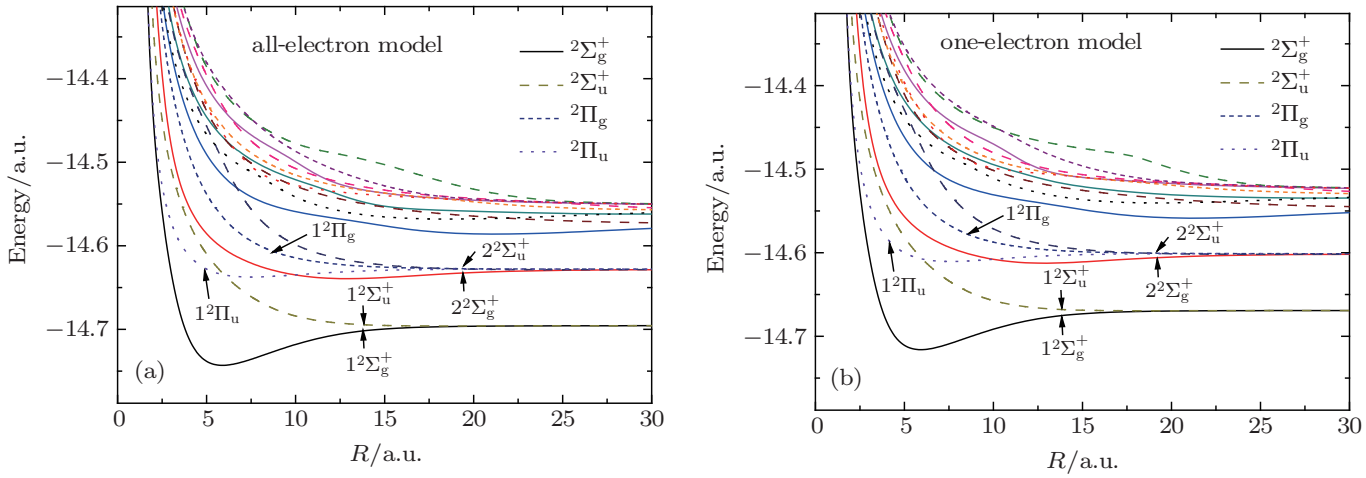


Fig. 1. (color online) Curves of potential energy versus internuclear distance R of the Li_2^+ molecular ion. (a) AEM; (b) OEM.

Table 1. Values of equilibrium position R_e (a.u.) and depth of potential well D_e (eV) for the lowest states of Li_2^+.

State	Present work				Ref. [18]		Ref. [19]		Ref. [20]		Ref. [7]	
	AEM		OEM									
	R_e	D_e	R_e	D_e	R_e	D_e	R_e	D_e	R_e	D_e	R_e	D_e
$1^2\Sigma_g^+$	5.90	1.293	5.90	1.278	5.98	1.26	5.90	1.31	5.94	1.24	5.89	1.248
$2^2\Sigma_g^+$	13.0	0.306	13.0	0.304	13.0	0.31	12.8	0.30				
$3^2\Sigma_g^+$	21.0	0.369	21.0	0.366	22.0	0.37						
$4^2\Sigma_g^+$	29.0	0.183	29.0	0.175	28.0	0.14						
$1^2\Sigma_u^+$	19.0	0.0116	19.0	0.0111	19.0	0.011	18.0	0.011				
$2^2\Sigma_u^+$	25.0	0.0160	25.0	0.0150	25.0	0.016	24.0	0.014				
$3^2\Sigma_u^+$	37.0	0.0219	38.0	0.0187								
$4^2\Sigma_u^+$	42.0	0.0552	45.0	0.0497								
$2^2\Pi_g$	35.0	0.052	36.5	0.0459								
$1^2\Pi_u$	7.50	0.255	7.50	0.249	7.60	0.25	7.60	0.35	8.26	0.17		
$2^2\Pi_u$	18.5	0.345	19.0	0.332	19.5	0.37						

The radial coupling matrix elements are shown in Fig. 2 for the g-states (Fig. 2(a)) in the all-electron model and Fig. 2(c) in the one-electron model) and u-states (Fig. 2(b) in the all-electron model and Fig. 2(d) in the one-electron model) of the system with the electron translation factors included. We can see that the results of the all-electron model and the one-electron model are very similar except for the couplings between the higher states at small internuclear distances. This would have some influence on the cross sections only in the high collision energy region. The $1^2\Sigma_g^+$ and $1^2\Sigma_u^+$ states do not couple with upper states strongly until $R < 5$ a.u. This means that the state couplings would only influence the resonant charge transfer process at very high energies. The two-state approximation would be adequate in the low energy region.

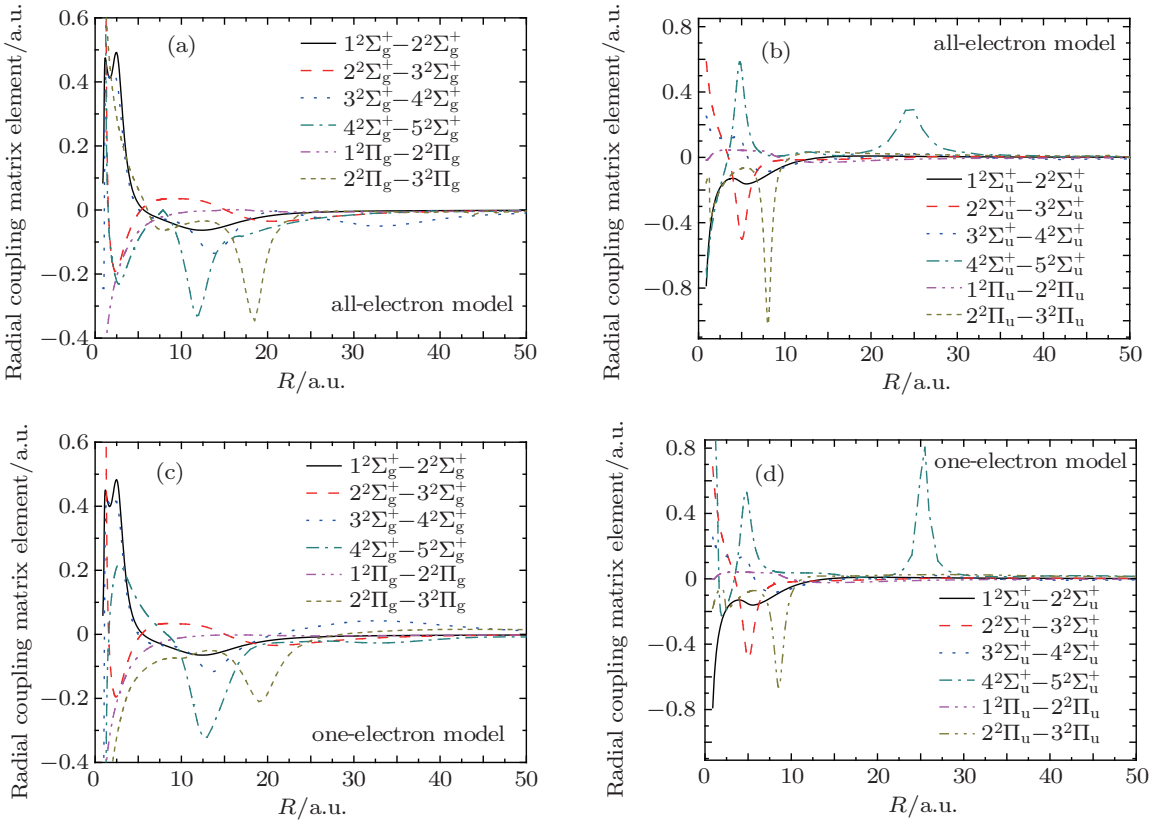


Fig. 2. (color online) Radial coupling matrix elements between the g-states (panels (a) and (c)) and between the u-states (panels (b) and (d)) of Li_2^+.

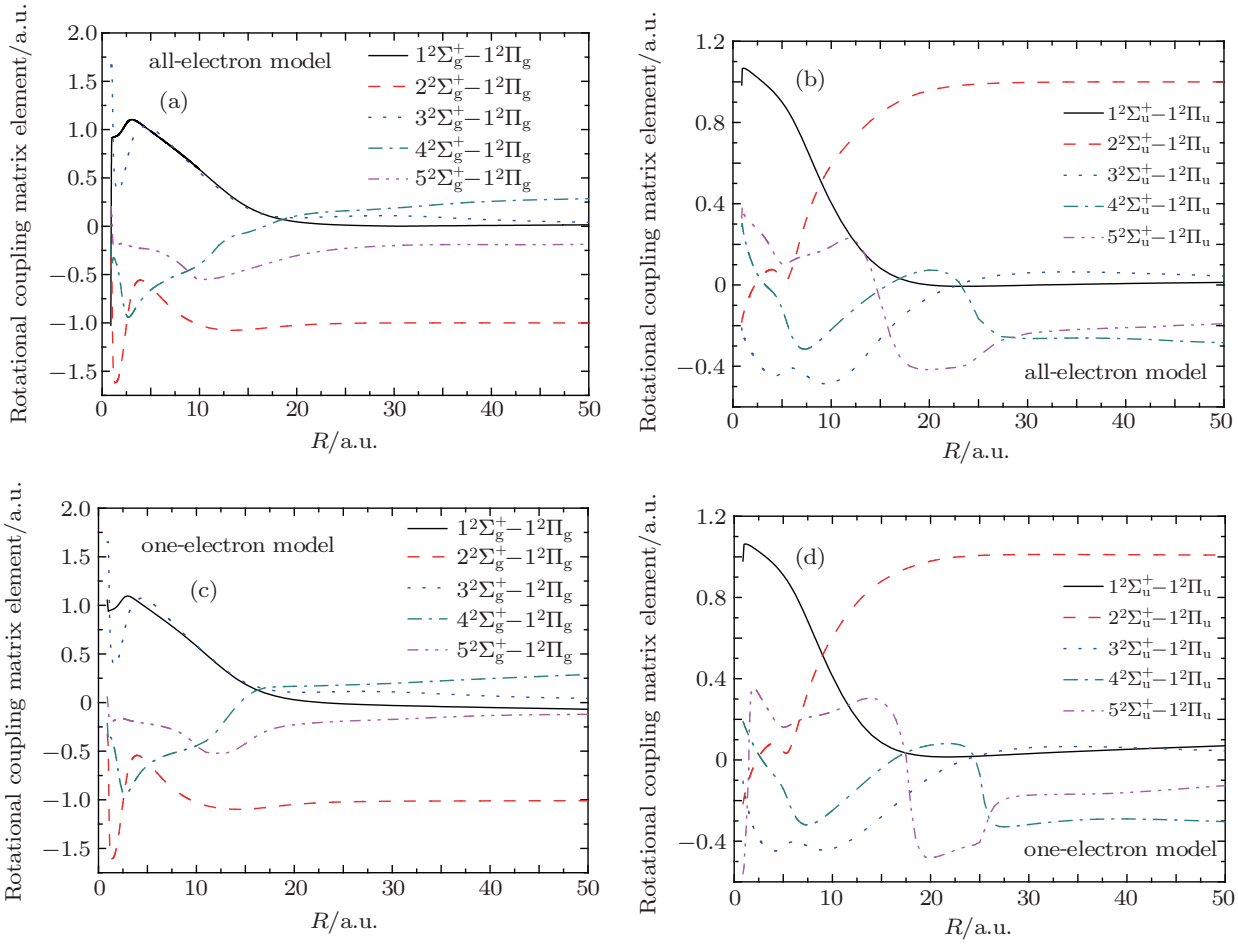


Fig. 3. (color online) Rotational coupling matrix elements between the g-states ((a) and (c)) and between the u-states ((b) and (d)) of Li_2^+.

3.2. Cross sections

The present resonant charge transfer cross sections calculated by the QMOCC method in an energy range of 1.0 eV/u–5000 eV/u, and by the TC-AOCC method in an energy range of 100 eV/u–10^4 eV/u are shown in Fig. 4. In the same figure, we also show Lorents *et al.*'s[1] and Perel *et al.*'s[2] experimental results, as well as Allan and Hanssen's theoretical results.[6] obtained with the 12-state SMOCC method, Men *et al.*'s[7] and McMillan's[5] 3-state SMOCC results, and Peek *et al.*'s[4] 2-state SMOCC results. The results of the present QMOCC calculations (AEM and OEM) and AOCC calculation agree well with each other at energies around 1 keV/u, where the two theoretical methods are both reliable.

Our OEM results are slightly larger than those of the AEM calculation in the whole energy range. For energies below 1 keV/u the relative discrepancies between the results of the two models are within 12%, however, with increasing collision energies the relative discrepancies will increase. This is because the cross sections sensitively depend on the accuracy of the molecular structures, and at small internuclear distances their OEM and AEM calculations are slightly different from each other. For energies below 1 keV/u the OEM calculation can also give a reliable prediction of the resonant charge transfer cross sections for the Li^+–Li collision system, while at energies above 1 keV/u it becomes unreliable since the model potential and pseudopotential energies lack the repulsive core which becomes important in the high-energy region.

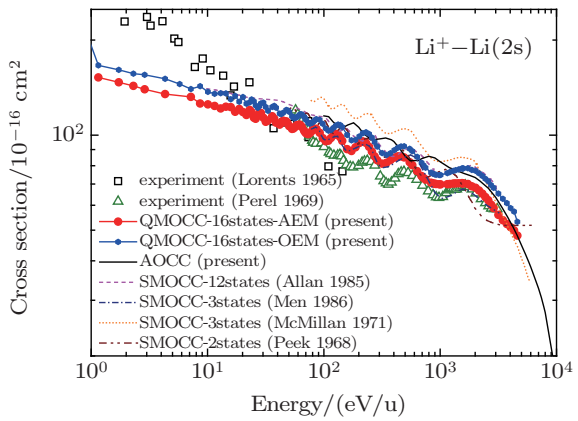


Fig. 4. (color online) Plots of resonant charge transfer cross section versus energy for Li^+–Li(2s) collisions.

Our QMOCC and AOCC calculations also agree well with most of the other theoretical results.[4–7] The charge transfer cross sections decrease with the increasing of energy, but all of the experimental and theoretical results show oscillation structures in an energy range of 10 eV/u–5000 eV/u. The potential energy curves at small internuclear distances critically influence the forms of these oscillations, which results from the collisions at small impact parameters. The three-state results of McMillan[5] are larger than other calculations. This may arise from their inaccurate molecular structures, as we have noted that the magnitudes of the cross sections depend sensitively on the molecular structure calculations. For energies above 1 keV/u, serious discrepancies can be observed between the SMOCC results of Peek[4] and other calculations. This may be due to the two-state approximation used in their SMOCC calculation. The inelastic transition at small internuclear distance (see Figs. 1–3), which has been proved to be important for the results in the high collision energy region, was not taken into account in their calculations. Men *et al.*[7] also performed the two-state calculation and showed that the two-state and three-state results have similar magnitudes, but the frequencies of the oscillation structures are different at about $E > 200$ eV/u.

For energies above 20 eV/u, the present AEM cross sections agree well with the experimental measurements,[1,2] with no more than 20% discrepancies. The oscillatory structures measured by Perel *et al.*[2] are very well reproduced in our calculations. For energies below 20 eV/u, the resonant charge transfer cross sections measured by Lorents *et al.*[6] are quite different from ours and other theoretical results.[1] More accurate absolute experiments are desirable to resolve this remaining question.

4. Conclusions

In this paper, accurate molecular structure data are calculated with AEM by the MRDCI method for the Li^+–Li(2s) collision. The QMOCC and AOCC methods are employed to calculate the resonant charge transfer cross sections in energy ranges of 1.0 eV/u–5000 eV/u and 100 eV/u–104 eV/u, respectively. Our QMOCC calculations are carried out with AEM and OEM, respectively. The comparison between the results of the two models indicates that OEM calculation can also give a reliable prediction of the resonant charge transfer cross sections at energies below 1 keV/u. At higher energies, the influence of core electrons should be taken into account. The oscillatory structures observed in experiments are very well reproduced by our calculations. In an energy region of $E < 20$ eV/u, the theoretical results are smaller than the experiment measurements and more accurate experiments are desired in this energy region.

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