Theoretical Study of Alignment and Orientation in $Li^+ + He$ Collisions

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This paper reports the first theoretical calculations of alignment and orientation of the electron cloud of the $Li(2^2P)$ and $He(2^1P)$ states excited by $2p\sigma$-$2p\pi$ rotational coupling in $Li^+ + He$ collisions at energies from 0.8 to 25 keV. The molecular-orbital-expansion method is used with specific inclusion of the molecular-electron-translation factor. Calculations made with this method are found to be in very good accord with the recent measurement.

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Recently, impressive experimental progress on coherence analysis and the angular-correlation study of the electron cloud in ion-atom collisions has provided deeper insight into the collision dynamics.[1] In particular, these experiments have been able to visualize the orientation and alignment of the electron cloud of excited states produced by a collision event. These measurements provide clear and specific information on the state-coupling scheme that dominates the collision dynamics. Among recent important experiments, Andersen *et al.*[2] have reported $Li(2^2P)$ and $He(2^1P)$ orientation and alignment studies in $Li^+ + He$ collisions in the energy range from 1 to 25 keV. The competing charge-transfer and excitation processes leading to the $Li(2^2P)$ and $He(2^1P)$ excited states, respectively, are particularly well suited to testing alternative theoretical prescriptions for the electron-translation factor (ETF), since the most important dynamics occur at small internuclear separations. The measurements are extremely interesting, from a theoretical point of view, particularly with regard to the following points[3]:

(i) Below the collision energy of approximately 5 keV, the shape of the electron cloud is very nearly that of a p orbital, aligned perpendicular to the asymptotic internuclear axis, independent of whether the electron stays on the He atom or is transferred to the Li atom.

(ii) As the collision energy is increased above 5 keV, the shape is observed to change from that of a pure p orbital. The alignment angle γ deviates from the perpendicular direction to that of the asymptotic internuclear axis, γ being larger than 90° for Li and smaller than 90° for He. This experimental finding is a strong contradiction to the prediction by simple theories.

(iii) The angular momentum $\langle L_\perp \rangle$ component perpendicular to the collision plane shows a pronounced variation with collision energy, but is only weakly dependent on impact parameter.

At least one theoretical attempt using the molecular-orbital- (MO-) expansion method for understanding the collision dynamics for these observed phenomena has been made by Gala *et al.*[4] However, partly as a result of the non-Galilean-invariant nature[5] of their treatment of the scattering problem and partly as a result of the sensitivity of the results to the accuracy of the molecular wave functions used in the calculation, this treatment[4] did not provide an accurate theoretical interpretation of the experimental findings.

Since the experimental alignment and orientation studies[2] have been performed at very small impact parameters, between 0.2 and 1.1 a.u., it might be anticipated that very precise molecular wave functions at small internuclear separation ($R < 2$ a.u.) as well as a reasonably "good" representation of the molecular-electron-translation factors would be indispensable for an accurate description of this kind of phenomenon. We have calculated the $Li(2^2P)$ and $He(2^1P)$ alignment angles and the angular momentum components $\langle L_\perp \rangle$ in $Li^+ + He$ collisions at collision energies in the range of 0.8 to 25 keV by the MO-expansion method incorporating for the first time the molecular-ETF (MO-ETF) approach. Also, we have examined the sensitivity of these results to alternative choices for the analytic form of the ETF.

In the present work the pseudopotential method[6] has been employed to obtain the molecular wave function. In this method, the lithium core ($1s^2$ electrons) is replaced by the Gaussian-type l-dependent pseudopotential, while the two electrons of the He atom are treated explicitly. This approximate method is consistent with the fact that the two Li-core electrons are bound so tightly, compared to those in the He atom, that they are not significantly perturbed by the collision dynamics, in this energy region. However, the electrons on the He atom are active during the collision. The total nonrelativistic stationary electronic Hamiltonian has been constructed in the ordinary way for a two-electron, two-center system with a pseudopotential representing the Li core. This Hamiltonian was used to obtain molecular wave functions as well as eigenenergies. The scattering wave function was expanded as a product of a molecular wave function and an atomic or molecular ETF within the semiclassical formalism.[7] The form of the ETF is given by

$$F_i(\mathbf{r};R) = \exp[i\textstyle\sum_k \{\frac{1}{2} f_i(\mathbf{r}_k;R)\,\mathbf{v}\cdot\mathbf{r}_k - \frac{1}{8}\int^r v^2\,dt'\}], \quad (1)$$

where $\mathbf{v}$ is the relative velocity of the heavy particles, and $f_i(\mathbf{r}_k;R)$ represents a state-dependent switching function employed to assign a local propagation velocity, $f_i\mathbf{v}$, of the electron in the quasimolecule formed during the collision. For the ETF, in the present calculation, we have adopted two different forms: (i) atomic ETF (or plane-wave ETF)[8]—in which the f_i in Eq. (1) is chosen as ± 1 depending upon the nucleus to which the electron is attached; (ii) molecular ETF—in which the f_i in Eq. (1) is chosen as $f_i(\mathbf{r},R)=\tanh(R\beta_i\mathbf{r}_i)$, where β_i is a parameter which is determined so as to minimize nonadiabatic couplings.[9]

The standard procedure of semiclassical, impact-parameter collision theory is used to derive the familiar first-order coupled equations. Straight-line trajectories are assumed. By solving of these coupled equations numerically under specific initial conditions, the transition amplitudes for the various final states can be easily extracted. The alignment angle γ and the angular momentum $\langle L_\perp\rangle$ for the electron cloud are defined[10] by three Stokes parameters (P_1,P_2,P_3). These Stokes parameters are closely related to the transition amplitudes.[11]

In Fig. 1 we illustrate, schematically, the diabatic MO diagram (all seven states actually used in the present close-coupling calculation) for the $(\text{Li-He})^+$ system. Important radial- and rotational-coupling regions are indicated by circles and rectangles, respectively, along with corresponding relevant internuclear distances. From this diabatic picture, it may be expected that the flux initially in the ground state is promoted to the $2p\pi$ state which becomes degenerate with the ground state at the united-atom limit, being connected with the ground state through strong $2p\sigma$-$2p\pi$ rotational coupling. The narrow avoided crossing between the $2p\sigma$ and $2s\sigma$ states at $R\sim 0.42$ a.u. may

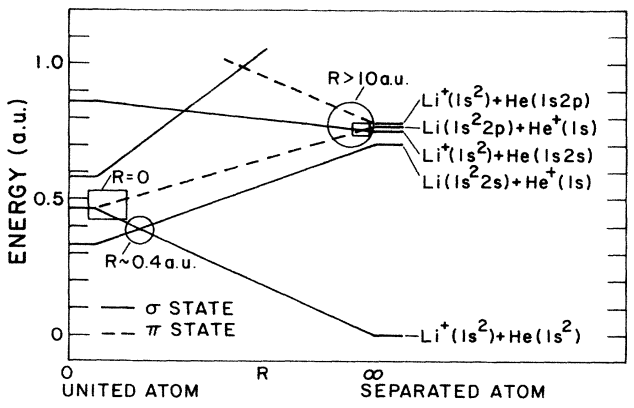

FIG. 1. A schematic diabatic MO diagram for the $(\text{Li-He})^+$ system. Important radial as well as rotational couplings are indicated by circles and rectangles, respectively, along with their regions.

also result in flux promotion, to some extent. However, as pointed out by Sidis, Stolterfoht, and Barat[12] the radial coupling between these states is rather weak and hence, the flux transfer to higher levels at this crossing may be a secondary process. The long-range π-π radial coupling between the $\text{Li}(2^2P_{\pm 1})+\text{He}^+$ and $\text{Li}^+ + \text{He}(2^1P_{\pm 1})$ levels at larger R plays an extremely important role in the flux redistribution between these states. Correspondingly, the rotational coupling between asymptotically degenerate states on the same atom also plays some part in the flux redistribution. Of course, these two coupling mechanisms are important only for the exit channel in the collision. Note that in the present calculation two-electron processes have been neglected.

Our calculated alignment angles γ_{Li} and γ_{He} are shown, as functions of collision energy, in Figs. 2(a) and 2(b), respectively, using (i) the molecular ETF—solid line in the figure—and (ii) the atomic ETF—broken line in the figure—along with the experimental measurement by Andersen *et al.*[2] The calculations were performed for a single impact parameter $b=0.55$ a.u., corresponding to the scattering angle selected in the measurements. The present molecular-ETF calculation reproduces the experimental trends very satisfactorily, while the calculation based on the atomic ETF agrees only in magnitude.

These comparisons strongly suggest that for such a small impact parameter, $b\simeq 0.55$ a.u., reasonably good molecular ETF's are necessary to describe correctly the electron-translational motion in the two-center field. Since the atomic ETF's do not allow for the essential two-center (molecular) character at small internuclear separations and this clearly reflects in the shape and magnitude of corresponding dynamical couplings, the atomic-ETF treatment cannot describe the collision dynamics correctly in the small-impact-parameter region. (See for example, Ref. 9c for the ETF effect for a one-electron system.) This fact is responsible for the differences between the molecular ETF and the atomic ETF in the figure. In our view, these comparisons provide very important additional information to the ETF dialogue which has been ongoing for many years.[7b]

The oscillatory structure seen in the energy dependence of the alignment angle γ arises from the passage of the phase χ (Ref. 11) through π due to strong coupling between the two near-degenerate channels which correlate to the $\text{Li}(2^2P)+\text{He}^+$ and $\text{Li}^+ + \text{He}(2^1P)$ levels. Therefore, the probabilities for $2p\sigma$ and $2p\pi$ states corresponding to these two channels are strongly energy dependent. In the molecular picture, the charge-transfer and excitation processes are closely related. When two ions or atoms approach sufficiently closely that they form a quasimolecule, then the electron cloud is shared by these two particles. As the par-

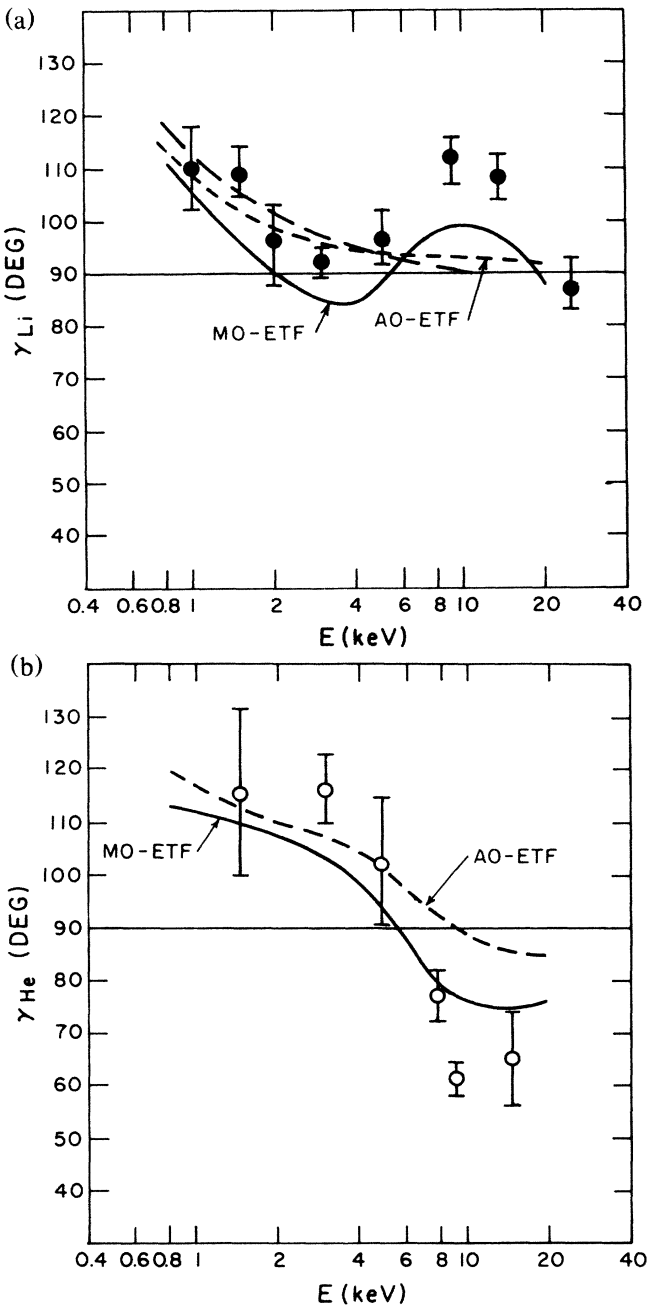

FIG. 2. (a) The alignment angle γ for Li calculated at impact parameter $b = 0.55$ a.u. as a function of energy E. Theory, solid line, MO-ETF; dashed line, atomic ETF; long-dashed line, direction perpendicular to the asymptotic internuclear axis. Experiment, circles, Andersen *et al.* (Ref. 2). (b) The same as in (a) except for He.

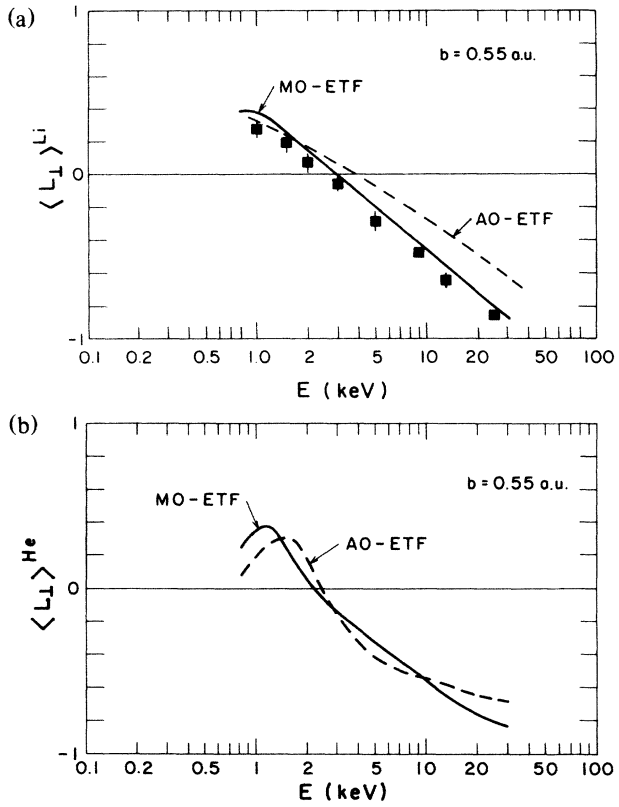

FIG. 3. (a) Transferred angular momentum $\langle L_\perp \rangle$ for Li as a function of energy. Theory, solid line, MO-ETF; dashed line, atomic ETF. Experiment, squares, Andersen *et al.* (Ref. 2). (b) The same as in (a) except for He.

ticles separate following the collision, it follows that if the projectile has a maximum probability for the electron distribution being located around it, then the target has a minimum, and vice versa. Therefore, the probability of the charge transfer should be out of phase with that of the excitation. This simple picture illustrates qualitatively the physical explanation of the out-of-phase phenomenon in the alignment angles γ_{Li} and γ_{He}.

In Figs. 3(a) and 3(b), the angular momentum $\langle L_\perp \rangle$ of the electron cloud is plotted along with the measurement of Andersen *et al.*[2] for Li and for He. Our theoretical result calculated at $b = 0.55$ reproduces the experimental findings nicely. The calculated results for $\langle L_\perp \rangle$ vary monotonically from 0.39 at 0.8 keV to -0.80 at 25 keV, changing its sign around $E \simeq 3.5$ keV for Li. This indicates that the potential becomes effectively repulsive as the collision energy increases. This comes from the sign change of $\sin\chi$ which makes $\langle L_\perp \rangle$ negative at higher energies. A similar reason can be given for the less satisfactory result observed in the atomic-ETF calculation. The remaining discrepancies observed between the theory and the experiment in the figures might be due partly to the lack of accuracy of the MO wave function and the ETF's and partly to the experiment.[2]

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[3]Measurements by Andersen *et al.* (Ref. 2) concentrate particularly on the alignment angle γ and the angular momentum $\langle L_\perp \rangle$ of the excited electron cloud in the collision. The alignment angle γ is defined as the angle formed between the major symmetry axis of the electron charge cloud and the axis parallel to the incoming particle direction on the scattering plane, and $\langle L_\perp \rangle$ is the angular momentum component perpendicular to the scattering plane.

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[5]For correct treatment of the molecular-orbital-expansion method, the electron-translation factor has to included in the scattering wave function within a semiclassical formalism. If the ETF is omitted from the scattering wave function, it cannot satisfy correct scattering boundary conditions and hence is not Galilean invariant.

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$$P_1 = 2\lambda - 1, \quad P_2 = -2[\lambda(1-\lambda)]^{1/2}\cos\chi,$$

$$P_3 = 2[\lambda(1-\lambda)]^{1/2}\sin\chi,$$

where

$$\lambda = |a_\sigma|^2/(|a_\sigma|^2 + |a_\pi|^2), \quad \chi = \arg(a_\pi/a_\sigma),$$

with a_σ and a_π being σ and π state amplitudes, respectively.

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