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Dynamical theory of the conversion among the state multipoles in the collisions of hydrogenlike species with ions

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The time evolution formula of state multipoles for states of hydrogenic ions in interaction with other ions is obtained in a rotating frame using an orthogonal-operator expansion. Our formula relates final-state multipoles to state multipoles of hydrogenic ions at earlier times. The theory is applied to the $n=2$ levels of hydrogen.

I. INTRODUCTION

It has long been recognized that outgoing ions that have excited atoms by collisions may give rise to postcollisional effects.[1] The field of outgoing ions causes transitions, in general, among the multiplets of close-lying states and alters the electron cloud distributions of excited atoms. Analyses of such phenomena are needed to extract information on the dynamics of collision because a comprehensive understanding of collision dynamics must incorporate the manifestations of the shape of electron clouds. In the present paper, we study such final-state interactions for hydrogen atoms excited by ion impact. The excited states of hydrogen have received considerable attention and coincidence data have become available within the last decade. The atomic charge cloud in this case exhibits geometric and dynamical anisotropies including static dipole moments as measured recently by Havener *et al.* for the H^++He electron capture reaction.[2]

Impact excitation of atoms generally leaves them in anisotropic states and the fields of outgoing ions will cause redistributions of these anisotropies. These anisotropies and their time evolution are most conveniently described by state multipoles.[3-9] Specifically for hydrogen, we have two convenient choices. One set of multipoles is suggested by Blum and Kleinpoppen who adapted earlier work by Fano in nuclear physics[3] and employed state multipole operators with mixed angular momenta $T_q^{[k]}(n;l'l)$.[4-6] The other set $T_q^{[k]}(j;k_1k_2)$, discussed recently by Burgdörfer,[8,9] is based on the dynamical symmetry group O(4) of a nonrelativistic hydrogen atom. The latter set is convenient for processes where there is an axis of symmetry, such as atoms in external, possibly dynamical fields. However, it seems that the former scheme is more intuitive since the hydrogen atom is more commonly described in a mixed angular scheme $|nlm\rangle$ instead of pseudospin eigenstates $|j_1u_1j_2u_2\rangle$. The $|nlm\rangle$ scheme is also more appropriate in the collision complex region. There exist definite linear relations between the two sets since both are complete bases for hydrogen multiplets. Therefore one can perform calculations in either scheme, and then make transformations to the other representation if desired.

The objective of this paper is to obtain the general conversion coefficients $G_n[(L'L)KQt_0,(l'l)kqt]$, which describe the conversion of state multipoles $\langle T_Q^{[K]}(n;L'L)^+\rangle_{t_0}$ at time t_0 to $\langle T_q^{[k]}(n;\,l'l)^+\rangle_t$ at time t under the influence of the field of an outgoing ion. In Sec. II we briefly review the Coulomb degeneracy and associated tensor operator sets, and prove that the time evolution coefficients $G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]$ of the O(4) scheme and $G_n[(L'L)KQt_0,(l'l)kqt]$ of the L scheme are related to each other by a linear transformation with coefficients given in terms of recoupling coefficients of four angular momenta. The physical model is described in Sec. III. The main task of the present paper, obtaining explicit expressions for the conversion coefficients, is done in Sec. IV. In Sec. V we shall apply our theory to $n=2$ excitation for the process $P^++H\rightarrow P^++H^*$ ($n=2$), where P^+ is a singly charged ion, and for the problem of a fast proton passing by an initially excited hydrogen atom at large impact parameter. The latter approach might be applied to the process of a proton passing through a crystal.

II. GENERAL THEORY

A. Coulomb degeneracy and multipole operators

The orbital angular momentum, $\mathbf{L}=\mathbf{r}\times\mathbf{p}$, and Rung-Lenz vector, $\mathbf{A}=(\mathbf{p}\times\mathbf{L}-\mathbf{L}\times\mathbf{p})/2-Z_T\mathbf{r}/r$, are two constants of motion in the hydrogenic species. Here we anticipate applications to collisions where a target T of charge Z_T interacts with a projectile P of charge Z_P and the population of the excited states of the target are altered by the interaction. Our results also apply to states populated by electron capture provided the subscripts T and P are interchanged. Within the subspace of bound states of energy E_n we introduce $\mathbf{K}=\mathbf{A}(Z_T^2/2|E_n|)^{1/2}$ and define the pseudospins $\mathbf{J}_1$ and $\mathbf{J}_2$;

$$\mathbf{J}_1=(\mathbf{L}+\mathbf{K})/2,\quad J_2=(\mathbf{L}-\mathbf{K})/2\ . \tag{1}$$

The invariant group for a bound-state multiplet of hydrogen is SO(4), isomorphic to $O_3\times O_3$, with $\mathbf{J}_1$ and $\mathbf{J}_2$ as the group generators of corresponding O_3 space. In this group space, $j_1^2=j_2^2=j(j+1)$, and the following useful relation holds:[10,11]

$$\mathbf{r}=\mathbf{A}(3Z_T/4|E_n|)=\mathbf{K}(3n/2Z_T)\ . \tag{2}$$

The states of hydrogenic species are thus described in two different ways. One way is to use ordinary eigenvectors $|nlm\rangle$ which are the eigenstates of $H,\mathbf{L}^2$, and L_z. The other is to use $|ju_1ju_2\rangle$ which are the eigenstates of H, J_{1z}, and J_{2z} (i.e., the eigenstates of $\mathbf{J}_1^2$, $\mathbf{J}_2^2$, J_{1z}, and J_{2z}). Since $\mathbf{L}=\mathbf{J}_1+\mathbf{J}_2$, the change from one description to another is accomplished by the addition of two angular momenta. Similarly, multipole operators for a multiplet can be constructed in two alternative ways. The first set, the L multipole operators, are constructed from the state vectors $|nlm\rangle$ with the definition[4–6]

$$T_q^{[k]}(n;l'l)=\sum_{m,m'}(-1)^{l-m}\langle l'm'l-m|l'lkq\rangle \times|l'm'\rangle\langle lm|\ , \tag{3}$$

and the second set, O(4) multipole operators, are defined through pseudospin states $|ju_1ju_2\rangle$ as

$$\begin{aligned}T_q^{[k]}(j;k_1k_2)&=[T^{[k_1]}(j)\times T^{[k_2]}(j)]_q^{[k]}\\&=\sum_{q_1,q_2}\langle k_1q_1k_2q_2|k_1k_2kq\rangle\\&\qquad\times T_{q_1}^{[k_1]}(j)T_{q_2}^{[k_2]}(j)\ ,\end{aligned} \tag{4}$$

where $j=(n-1)/2$, and $T^{[k_1]}(j)$ and $T^{[k_2]}(j)$ are multipole operators defined in the corresponding O_3 space. These operators form an orthogonal set and satisfy the orthogonal relation

$$\mathrm{Tr}[T_{q'}^{[k']}(j;k_1'k_2')^\dagger T_q^{[k]}(j;k_1k_2)]=\delta_{k_1'k_1}\delta_{k_2'k_2}\delta_{k'k}\delta_{q'q}\ . \tag{5}$$

The two types of operators $T_q^{[k]}(n;\ l'l)$ and $T_q^{[k]}(j;\ k_1k_2)$ are related by the recoupling transformations

$$T_q^{[k]}(n;l'l)=\sum_{k_1,k_2}\langle(jj)l',(jj)l,k|(jj)k_1,(jj)k_2,k\rangle \times T_q^{[k]}(j;k_1k_2) \tag{6}$$

and

$$T_q^{[k]}(j;k_1k_2)=\sum_{l',l}\langle(jj)l',(jj)l,k|(jj)k_1,(jj)k_2,k\rangle \times T_q^{[k]}(n;l'l)\ . \tag{7}$$

B. Perturbation coefficients

The general orthogonal-operator expansion technique is used to expand the density operator $\rho(t)$ of the system at a time t in terms of the O(4) tensor set, i.e.,

$$\rho(t)=\sum_{k,q}\sum_{k_1,k_2}\langle T_q^{[k]}(j;k_1k_2)^\dagger\rangle_t T_q^{[k]}(j;k_1k_2)\ , \tag{8}$$

with the expansion coefficients, the O(4) multipoles, given by

$$\langle T_q^{[k]}(j;k_1k_2)^\dagger\rangle_t=\mathrm{Tr}[\rho(t)T_q^{[k]}(j;k_1k_2)^\dagger]\ . \tag{9}$$

The time evolution operator $U(t,t_0)$ of the system relates $\rho(t)$ and $\rho(t_0)$ through the relation $\rho(t)=U(t,t_0)\rho(t_0)U^\dagger(t,t_0)$, thus the multipoles $\langle T_q^{[k]}(j;k_1k_2)^\dagger\rangle_t$ at a time t relate to multipoles $\langle T_Q^{[K]}(j;K_1K_2)^\dagger\rangle_{t_0}$ at t_0, according to

$$\begin{aligned}\langle T_q^{[k]}(j;k_1k_2)^\dagger\rangle_t&=\mathrm{Tr}[\rho(t)T_q^{[k]}(j;k_1k_2)^\dagger]=\mathrm{Tr}[U(t,t_0)\rho(t_0)U^\dagger(t,t_0)T_q^{[k]}(j;k_1k_2)^\dagger]\\&=\sum_{K,Q}\sum_{K_1,K_2}\langle T_q^{[K]}(j;K_1K_2)^\dagger\rangle_{t_0}G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]\ ,\end{aligned} \tag{10}$$

where the perturbation coefficients are given by

$$G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]=\mathrm{Tr}[U(t,t_0)T_q^{[k]}(j;K_1K_2)U^\dagger(t,t_0)T_q^{[k]}(j;k_1k_2)^\dagger]\ . \tag{11}$$

Alternatively, the density operator at a time t can be also expanded in terms of the tensor sets of Eq. (3). The perturbation coefficients in this case are obtained by using the transformation of Eq. (6) in Eq. (11); we have

$$\begin{aligned}G_n[(L'L)t_0,(l'l)kqt]=\sum_{K_1,K_2}\sum_{k_1,k_2}&\langle(jj)L',(jj)L,K|(jj)K_1,(jj)K_2,K\rangle\\&\times\langle(jj)l',(jj)l,k|(jj)k_1,(jj)k_2,k\rangle G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]\ ,\end{aligned} \tag{12}$$

and inversely

$$\begin{aligned}G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]=\sum_{L',L}\sum_{l',l}&\langle(jj)L',(jj)L,K|(jj)K_1,(jj)K_2,K\rangle\\&\times\langle(jj)l',(jj)l,k|(jj)k_1,(jj)k_2,k\rangle G_n[(L'L)KQt_0,(l'l)kqt]\ .\end{aligned} \tag{13}$$

Calculation of the coefficient $G_n[(L'L)KQt_0,(l'l)kqt]$ proceeds in three steps. Firstly, we compute the time evolution matrix $U(t,t_0)$ using a model described in Sec. III, then evaluate the coefficients in the O(4) representation using Eq. (11) and finally transform to the L representation using Eq. (12).

III. PHYSICAL MODEL

The physical process is illustrated in Fig. 1. An incident ion excites the target hydrogen so that for $t>t_0$ the atom is in the nth level. After excitation the electron cloud evolves under the influence of the field of the outgoing ion acting on the target. The evolution is described by time-dependent state multipoles; in our discussion we neglect the much less likely transitions among states of different principal quantum number n. The projectile is treated as a classical particle moving with a definite velocity and impact parameter b in the central field of the target. We choose the plane of orbit as the XZ plane, and the rotating internuclear axis as the quantization axis of the hydrogen wave functions.[12] Thus, in the dipole approximation, the perturbation Hamiltonian is written as

$$H'=(-Z_P z+bvL_y)/R^2(t) , \tag{14}$$

where Z_P is the charge of the projectile. In obtaining Eq. (14), we have used the conservation of angular momentum of the projectile, that is, $R^2(t)\dot{\theta}(t)=-bv$. Substituting Eqs. (1) and (2) into Eq. (14) we have for the model Hamiltonian the result

$$\begin{aligned} H'=[&(-3nZ_P\hat{\mathbf{z}}/2Z_T+bv\hat{\mathbf{y}})\cdot\mathbf{J}_1 \\ &+(3nZ_P\hat{\mathbf{z}}/2Z_T+bv\hat{\mathbf{y}})\cdot\mathbf{J}_2]/R^2(t) . \end{aligned} \tag{15}$$

The interaction Hamiltonian H_I' in the interaction picture equals H'. Furthermore, $\mathbf{J}_1$ and $\mathbf{J}_2$ commute with the unperturbed Hamiltonian. Thus we have the time evolution operator in the interaction picture,

$$\begin{aligned} U(t,t_0)&= \exp[i\omega(t,t_0)\mathbf{n}_1\cdot\mathbf{J}_1]\exp[-i\omega(t,t_0)\mathbf{n}_2\cdot\mathbf{J}_2] \\ &=U_1(t,t_0)U_2(t,t_0) , \end{aligned} \tag{16}$$

where

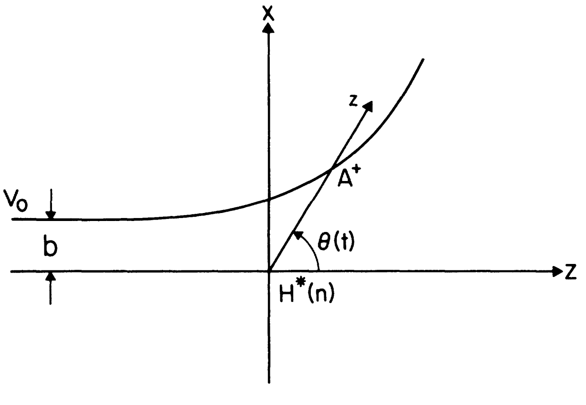

FIG. 1. Classical description of collision process.

$$U_1(t,t_0)= \exp[i\omega(t,t_0)\mathbf{n}_1\cdot\mathbf{J}_1] , \tag{17}$$

$$U_2(t,t_0)= \exp[i\omega(t,t_0)\mathbf{n}_2\cdot\mathbf{J}_2] , \tag{18}$$

$$\omega(t,t_0)=[(3nZ_P/2Z_T)^2+(bv)^2]^{1/2}\int_{t_0}^{t}\frac{dt}{R^2(t)} , \tag{19}$$

$$\mathbf{n}_1=(3nZ_P\hat{\mathbf{z}}/2Z_T-bv\hat{\mathbf{y}})/[(3nZ_P/2Z_T)^2+(bv)^2]^{1/2} , \tag{20}$$

and

$$\mathbf{n}_2=(3nZ_P\hat{\mathbf{z}}/2Z_T+bv\hat{\mathbf{y}})/[(3nZ_P/2Z_T)^2+(bv)^2]^{-1/2} . \tag{21}$$

The operators $U_1(t,t_0)$ and $U_2(t,t_0)$ in Eqs. (17) and (18) are written in the Euler angle representation according to Eqs. (12.11.8)–(12.11.11) of Ref. 13,

$$\begin{aligned} U_1(t,t_0)=&\exp[i\alpha(t,t_0)J_{1z}]\exp[i\beta(t,t_0)J_{1y}] \\ &\times\exp[i\alpha(t,t_0)J_{1z}] , \end{aligned} \tag{22}$$

$$\begin{aligned} U_2(t,t_0)=&\exp[-i\alpha(t,t_0)J_{2z}]\exp[i\beta(t,t_0)J_{2y}] \\ &\times\exp[-i\alpha(t,t_0)J_{2z}] , \end{aligned} \tag{23}$$

with

$$\beta(t,t_0)=-2\sin^{-1}\frac{\sin(\omega/2)}{[1+(3nZ_P/2Z_Tbv)^2]^{1/2}} \tag{24}$$

and

$$\alpha(t,t_0)=\sin^{-1}\frac{\sin(\omega/2)}{\cos(\beta/2)[1+(3nZ_P/2Z_Tbv)^2]^{1/2}} . \tag{25}$$

Since $1/R^2(t)=-\dot{\theta}(t)/bv$, we have that

$$\int_{t_0}^{t}\frac{dt}{R^2(t)}=[\theta(t)-\theta(t_0)]/bv . \tag{26}$$

The quantity $\theta(t)$ is determined by the particle trajectory. For the Coulomb potential $V(R)=Z_PZ_T/R(t)$ the angle $\theta(t)$ is easily calculated.[14] When t_0 corresponds to the distance of closest approach, this yields

$$\begin{aligned} \omega=&[1+(3nZ_P/2Z_Tbv)^2]^{1/2} \\ &\times\left[\frac{\pi}{2}-\sin^{-1}\frac{1}{[1+(2bE/Z_TZ_P)^2]^{1/2}}\right] . \end{aligned} \tag{27}$$

For energies of the order of 1 keV, $Z_PZ_T\sim 1$, and impact parameters of order of 1 a.u. the trajectory closely approximates a straight line so that the $\sin^{-1}$ term above is negligible.

With the time evolution matrix fully determined in this model it is now possible to compute the perturbation coefficients of Eqs. (11) and (12) in closed form. This is done in Sec. III.

IV. CALCULATION OF THE PERTURBATION COEFFICIENTS

A. General case

It is seen that the time evolution operator (16) is just a rotation in $O_3 \times O_3$ space with $U_1(t,t_0)$ and $U_2(t,t_0)$ operating on different O_3 spaces. Thus the O(4) scheme affords a simple means to compute the perturbation coefficients for our physical problem using standard angular momentum algebra. Substituting Eqs. (4) and (16) into Eq. (11), we readily obtain the perturbation coefficients in the O(4) scheme,

$$
\begin{aligned}
G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]
&=\delta_{K_1k_1}\delta_{K_2k_2}\sum_{Q_1',Q_2'}\sum_{Q_1Q_2}\langle K_1Q_1K_2Q_2|K_1K_2KQ\rangle\langle K_1Q_1'K_2Q_2'|K_1K_2kq\rangle \\
&\qquad\times D^{(K_1)}_{Q_1'Q_1}(\alpha,\beta,\alpha)D^{(K_2)}_{Q_2'Q_2}(-\alpha,\beta,-\alpha) \qquad (28)\\
&=\delta_{K_1k_1}\delta_{K_2k_2}\sum_{K'}\sum_{M',M}D^{(K')}_{M'M}(\alpha,\beta,\alpha) \\
&\qquad\times\sum_{Q_1',Q_2'}\sum_{Q_1,Q_2}(-1)^{Q_2'-Q_2}\langle K_1Q_1K_2Q_2|K_1K_2KQ\rangle\langle K_1Q_1K_2-Q_2|K_1K_2K'M\rangle \\
&\qquad\times\langle K_1Q_1'K_2Q_2'|K_1K_2kq\rangle\langle K_1Q_1'K_2-Q_2'|K_1K_2K'M'\rangle \ , \qquad (29)
\end{aligned}
$$

where we have used Eqs. (4.2.7) and (4.3.1) of Edmonds.[15]

The symmetry of the system yields relations among different perturbation coefficients. By noting that $D^{(K)}_{-M'-M}(\alpha,\beta,\alpha)=(-1)^{M'-M}D^{(K)}_{M'M}(\alpha,\beta,\alpha)$ and $D^{(K)}_{MM'}(\alpha,\beta,\alpha)=(-1)^{M'-M}D^{(K)}_{M'M}(\alpha,\beta,\alpha)$, one can prove

$$
G_j[(K_2K_1)KQt_0,(k_2k_1)kqt] =(-1)^{K+k}G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]^* \ , \qquad (30)
$$

and

$$
G_j[(k_1k_2)kqt_0,(K_1K_2)KQt] =(-1)^{Q-q}G_j[(K_1K_2)KQt_0,(k_1k_2)kqt] \ . \qquad (31)
$$

When $k_1=k_2$, Eq. (30) restricts the perturbation coefficients with $K+k$ even to be real, and those for $K+k$ odd to be imaginary.

Our results are quite general and apply to situations, e.g., triple coincidence geometries which lack even a plane of symmetry. When there is a plane of symmetry, taken here to be the XZ plane, this symmetry and Hermiticity of the density matrix implies relation among the state multipoles,[4-9,16] but no simplification of the perturbation coefficients follow this higher symmetry. Alternatively, when there is cylindrical symmetry some simplification ensues, which will now be discussed.

B. Cylindrically symmetric system

The Hamiltonian (14) consists of two terms. The term $-Z_Pz/R^2(t)$ represents the electric field interaction, and $bvL_y/R^2(t)$ is a Coriolis term present because we work in a rotating frame. This term has the same form as a magnetic contribution. Both terms are cylindrically symmetric, but with respect to z and y axis, respectively.

When the internuclear axis does not rotate for $t > t_0$, or approximately, when the incident energy is so low that the adiabatic approximation holds, the magnetic term vanishes. In this case only coefficients with $Q=q$ are nonzero and we have

$$
\begin{aligned}
G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]
&=\delta_{K_1k_1}\delta_{K_2k_2}\sum_{Q_1,Q_2}\langle K_1Q_1K_2Q_2|K_1K_2KQ\rangle \\
&\qquad\times\langle K_1Q_1K_2Q_2|K_1K_2kq\rangle \\
&\qquad\times\exp[2i(Q_1-Q_2)\alpha] \ , \qquad (32)
\end{aligned}
$$

which represents the Stark effect. If we have cylindrical symmetry so that $\langle T^{[K]}_Q(j;K_1K_2)\rangle_{t_0}=0$, then by restricting $Q=q=0$ and $\beta(t,t_0)=0$, we reduce Eq. (28) to

$$
\begin{aligned}
G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]
&=\delta_{K_1k_1}\delta_{K_2k_2}\sum_{Q_1}\exp[i4Q_1\alpha(t,t_0)] \\
&\qquad\times\langle K_1Q_1K_2-Q_1|K_1K_2K0\rangle \\
&\qquad\times\langle K_1Q_2K_1-Q_1|K_1K_2k0\rangle \ . \qquad (33)
\end{aligned}
$$

We notice that the electric term will, in general, also contribute to the conversions among the multipole components even with $q=0$ when the z-axis symmetry is broken, i.e., when the magnetic term is not negligible.

The other special symmetric case, which occurs when the incident energy or impact parameter goes to infinity so that the electric term disappears, namely, $\alpha(t,t_0)=0$, is also of interest. This gives

$$
G_j[(K_1K_2)KQt_0,(k_1k_2)kqt] =\delta_{K_1k_1}\delta_{K_2k_2}\delta_{Kk}(-1)^{Q+q}D^{(K)}_{Qq}(0,\beta,0) \ . \qquad (34)
$$

Accordingly, the contribution of the magnetic terms are confined to transfers among the multipole components of the same rank. This remain true even when the electric term does not vanish. Blum has discussed this property of the magnetic type of interaction for sharp angular momentum states.[4]

In the extreme limiting case $\alpha(t,t_0)=\beta(t,t_0)=0$, the preceding three equations (29), (33), and (34) give identical results

$$G_j[(K_1K_2)KQt_0,(k_1k_2)kqt]=\delta_{K_1k_1}\delta_{K_2k_2}\delta_{Kk}\delta_{Qq} ,$$

that is, there is no transfer among the multipoles. This is, of course, reasonable since $\alpha(t,t_0)=\beta(t,t_0)=0$ means that the outgoing ion and the target do not interact.

Equations (10) and (11) relate the O(4) multipoles at a time t to their initial values. The transformation relation (12) and (13) bridge the two schemes, and enable us to interpret the results in the L scheme. These equations, together with Eq. (29), represent the main results of this work. In Sec. V we apply the theory to $n=2$ excitation of hydrogen.

V. APPLICATIONS

In this section we apply our result to the $n=2$ level of atomic hydrogen when there is a singly charged ion in the final state.

A. Relations between multipoles and the Fano-Macek parameters for $n=2$

The Fano-Macek orientation and alignment parameters are commonly used to describe the atomic anisotropy[17] so it would be useful for the application of the theory to present the relations between the state multipoles and these parameters. From Eq. (4.4.6) of Ref. (6) and Eq. (8), we obtain the relations for the $n=2$ levels,

$$\langle T^{[0]}_0(n;00)^+\rangle=\tfrac{1}{2}\langle T^{[0]}_0(j;00)^\dagger\rangle+\frac{\sqrt{3}}{2}\langle T^{[0]}_0(j;11)^\dagger\rangle$$

$$=\frac{\sigma(2s)}{\sigma(2s)+\sigma(2p)} , \qquad (35a)$$

$$\langle T^{[0]}_0(n;11)^+\rangle=\frac{\sqrt{3}}{2}\langle T^{[0]}_0(j;00)^\dagger\rangle-\tfrac{1}{2}\langle T^{[0]}_0(j;11)^\dagger\rangle$$

$$=\frac{\sigma(2p)}{\sigma(2s)+\sigma(2p)} , \qquad (35b)$$

$$\langle T^{[1]}_1(n;11)^+\rangle=\frac{1}{\sqrt{2}}\langle T^{[1]}_1(j;10)^\dagger\rangle$$

$$+\frac{1}{\sqrt{2}}\langle T^{[1]}_1(j;01)^\dagger\rangle$$

$$=-\frac{i\sigma(2p)O^{\mathrm{det})}_{1-}}{\sqrt{6}[\sigma(2s)+\sigma(2p)]} , \qquad (35c)$$

$$\langle T^{[2]}_0(n;11)^\dagger\rangle=\langle T^{[2]}_0(j;11)^\dagger\rangle=\left[\frac{2}{3}\right]^{1/2}\frac{\sigma(2p)A^{(\mathrm{det})}_0}{\sigma(2s)+\sigma(2p)} , \qquad (35d)$$

$$\langle T^{[2]}_1(n;11)^\dagger\rangle=\langle T^{[2]}_1(j;11)^\dagger\rangle=-\frac{\sigma(2p)A^{(\mathrm{det})}_{1+}}{\sigma(2s)+\sigma(2p)} , \qquad (35e)$$

$$\langle T^{[2]}_2(n;11)^\dagger\rangle=\langle T^{[2]}_2(j;11)^\dagger\rangle=\frac{\sigma(2p)A^{(\mathrm{det})}_{2+}}{\sigma(2s)+\sigma(2p)} , \qquad (35f)$$

$$\langle T^{[1]}_0(n;10)^\dagger\rangle=\frac{1}{\sqrt{2}}\langle T^{[1]}_0(j;11)^\dagger\rangle+\tfrac{1}{2}\langle T^{[1]}_0(j;10)^\dagger\rangle$$

$$-\tfrac{1}{2}\langle T^{[1]}_0(j;01)^\dagger\rangle=\rho_{2p_{m=0},2s} , \qquad (35g)$$

$$\langle T^{[1]}_1(n;10)^\dagger\rangle=\frac{1}{\sqrt{2}}\langle T^{[1]}_1(j;11)^\dagger\rangle+\tfrac{1}{2}\langle T^{[1]}_1(j;10)^\dagger\rangle$$

$$-\tfrac{1}{2}\langle T^{[1]}_1(j;01)^\dagger\rangle=\rho_{2p_{m=1},2s} , \qquad (35h)$$

where $\sigma(2s)$ and $\sigma(2p)$ are the differential cross sections for $2s$ and $2p$ states. Note that there are only eight independent L multipoles for $n=2$ excitation as a consequence of Hermiticity of the density matrix and reflection symmetry of the system through the scattering plane. The others are obtained from the relation $\langle T^{[k]}_{-q}(n;l'l)^\dagger\rangle=(-1)^{k+q+l+l'}\langle T^{[k]}_q(n;l'l)^+\rangle$.[5] In addition, two non-diagonal elements of the density matrix have been used to describe coherent $2s$-$2p$ states.

B. Perturbation coefficients for $n=2$

For $n=2$ the values of k_1 and k_2 in Eq. (4) are either 0 or 1 since $j=(n-1)/2=\frac{1}{2}$. The perturbation coefficients in the O(4) scheme are obtained from Eq. (29), and the coefficients in the L scheme are then computed using Eq. (12). In the following, we present the O(4) perturbation coefficients of interest. The others can be retrieved with the help of Eqs. (30) and (31). At the same time, the perturbation coefficients in the L scheme are written as a linear combination of those of O(4) scheme.

1. Transfers among the multipoles of the same rank

(i) For O(4) multipoles, we have

$$G_j[(00)00t_0,(k_1k_2)kqt]=\delta_{k_10}\delta_{k_20}\delta_{k0}\delta_{q0} , \qquad (36a)$$

$$G_j[(11)00t_0,(11)00t]=\tfrac{1}{3}\cos^2\beta+\tfrac{2}{3}\sin^2\beta\cos2\alpha$$

$$+(1-\cos\beta)^2+(1+\cos\beta)^2\cos4\alpha , \qquad (36b)$$

$$G_j[(10)10t_0,(10)11t]=\frac{1}{\sqrt{2}}\sin\beta\exp(i\alpha) , \qquad (36c)$$

$$G_j[(10)11t_0,(10)11t]=\tfrac{1}{2}(1+\cos\beta)\exp(i2\alpha) , \qquad (36d)$$

$$G_j(11)10t_0,(11)11t]=\frac{1}{2\sqrt{2}}\sin\beta[(1+\cos\beta)\cos3\alpha$$

$$+(1-\cos\beta)\cos\alpha] , \qquad (36e)$$

$$G_j[(11)20t_0,(11)21t] = \frac{1}{2\sqrt{6}}\sin\beta[(5\cos\beta-1)\cos\alpha+(1+\cos\beta)\cos3\alpha] , \tag{36f}$$

$$G_j[(11)20t_0,(11)22t]=\frac{1}{\sqrt{6}}\sin^2\beta(1+\tfrac{1}{2}\cos2\alpha) , \tag{36g}$$

$$G_j[(11)21t_0,(11)22t]=\tfrac{1}{2}\sin\beta(1+\cos\beta)\cos\alpha . \tag{36h}$$

(ii) For L multipoles, we have

$$G_n[(00)00t_0,(00)00t]=\tfrac{1}{4}(1+3G_j[(11)00t_0,(11)00t]) , \tag{36i}$$

$$G_n[(00)00t_0,(11)00t]=\tfrac{3}{4}(1-G_j[(11)00t_0,(11)00t]) , \tag{36j}$$

$$G_n[(11)00t_0,(11)00t]=\tfrac{1}{4}(3+G_j[(11)00,(11)00t]) , \tag{36k}$$

$$\begin{aligned}G_n[(10)10t_0,(10)11t]=&\tfrac{1}{2}G_j[(11)10t_0,(11)11t]\\ &+\tfrac{1}{4}G_j[(10)10t_0,(10)11t]\\ &+\tfrac{1}{4}G_j[(01)10t_0,(01)11t] ,\end{aligned} \tag{36l}$$

$$\begin{aligned}G_n[(10)1Qt_0,(11)11t] &= \frac{1}{2\sqrt{2}}\{G_j[(10)1Qt_0,(11)11t]\\ &\quad -G_j[(01)1Qt_0,(01)11t]\} \quad (Q=0,1) ,\end{aligned} \tag{36m}$$

$$G_n[(11)2Qt_0,(11)2qt]=G_j[(11)2Qt_0,(11)2qt] \quad (Q=0,1,2;\ q=0,1,2) . \tag{36n}$$

2. Transfer from the monopoles to k = 1 multipoles

(i) For O(4) multipoles, we have

$$G_j[(11)00t_0,(11)10t] = \frac{i}{\sqrt{6}}\sin2\alpha[\sin^2\beta+(1+\cos\beta)^2\cos2\alpha] , \tag{37a}$$

$$\begin{aligned}G_j[(11)00t_0,(11)11t] &= \frac{i}{2\sqrt{3}}\sin\beta[(1-3\cos\beta)\sin\alpha\\ &\quad +(1+\cos\beta)\sin3\alpha] .\end{aligned} \tag{37b}$$

(ii) For L multipoles, we have

$$G_n[(00)00t_0,(10)1qt]=\frac{\sqrt{3}}{2\sqrt{2}}G_j[(11)00t_0,(11)00t] \quad (q=0,1) , \tag{37c}$$

$$G_n[(00)00t_0,(11)11t]\equiv0 , \tag{37d}$$

$$G_n[(11)00t_0,(10)1qt]=-\frac{1}{2\sqrt{2}}G_j[(11)00t_0,(11)1qt] \quad (q=0,1) . \tag{37e}$$

3. Transfers from monopoles to k = 2 multipoles

(i) For O(4) multipoles, we have

$$\begin{aligned}G_j[(11)00t_0,(11)20t] &= \frac{1}{6\sqrt{2}}[(1-\cos\beta)^2-4\cos^2\beta-2\sin^2\beta\cos2\alpha\\ &\quad +(1+\cos\beta)\cos4\alpha] ,\end{aligned} \tag{38a}$$

$$\begin{aligned}G_j[(11)00t_0,(11)21t]=&\frac{1}{2\sqrt{2}}\sin\beta(1+\cos\beta)\\ &\times(\cos3\alpha-\cos\alpha) ,\end{aligned} \tag{38b}$$

$$G_j[(11)00t_0,(11)22t]=-\frac{1}{\sqrt{3}}\sin^2\beta\sin^2\alpha , \tag{38c}$$

(ii) For L multipoles, we have

$$G_n[(00)00t_0,(11)2qt]=-\tfrac{1}{2}G_j[(11)00t_0,(11)2qt] \quad (q=0,1,2) . \tag{38d}$$

4. Transfers from k = 1 to k = 2 multipoles

(i) For O(4) multipoles, we have

$$\begin{aligned}G_j[(11)10t_0,(11)20t]=&\frac{i}{4\sqrt{3}}[(1+\cos\beta)^2\sin4\alpha\\ &-\sin^2\beta\sin2\alpha] ,\end{aligned} \tag{39a}$$

$$\begin{aligned}G_j[(11)10t_0,(11)21t] &= \frac{i}{2\sqrt{2}}\sin\beta[(1+\cos\beta)\sin3\alpha\\ &\quad -(1-\cos\beta)\sin\alpha] ,\end{aligned} \tag{39b}$$

$$G_j[(11)10t_0,(11)22t]=\frac{i}{2\sqrt{2}}\sin^2\beta\sin2\alpha , \tag{39c}$$

$$\begin{aligned}G_j[(11)11t_0,(11)20t] &= -\frac{i}{2\sqrt{2}}[(1+3\cos\beta)\sin\beta\sin\alpha\\ &\quad +(1+\cos\beta)\sin3\alpha] ,\end{aligned} \tag{39d}$$

$$G_j[(11)11t_0,(11)21t]=\frac{i}{2}(1+\cos\beta)\cos\beta\sin2\alpha , \tag{39e}$$

$$G_j[(11)11t_0,(11)22t]=\frac{i}{2}(1+\cos\beta)\sin\beta\sin\alpha . \tag{39f}$$

(ii) For L multipoles, we have

$$G_n[(10)1Qt_0,(11)2qt]=\frac{1}{\sqrt{2}}G_j[(11)1Qt_0,(11)2qt] \quad (Q=0,1;\ q=0,1,2) , \tag{39g}$$

$$G_n[(11)11t_0,(11)2qt]\equiv0 \quad (q=0,1,2) . \tag{39h}$$

C. Numerical results

We consider a projectile of charge $+1$ passing a hydrogen atom in an $n=2$ level. Three perturbation coefficients $G_j[(k_1k_2)KQt_0,(k_1,k_2)kqt]$ are shown in the Fig. 2 as a function of the incident energy. The projectile is chosen to be He† and the impact parameter is $b=8$ a.u. The existence of nonzero perturbation coefficients indicate that conversions among the multipoles occur.

From Eqs. (35) it is clear that the orientation multipoles $\langle T_1^{[1]}](n;11)^\dagger\rangle$ are superposition of two O(4) multipoles with $k_1=1$, $k_2=0$ and $k_1=0$, $k_2=1$. On the other hand, the monopoles of $2s$ and $2p$, and the alignment multipoles relate only to the O(4) multipoles with $k_1=k_2=1$. Therefore the selection rules $k_1=K_1$ and $k_2=K_2$ in Eq. (29) strictly prohibit transfers to (from) the $2p$ orientation $\langle T_1^{[1]}(n;11)^\dagger\rangle$ from (to) the $2s$ and $2p$ monopoles $\langle T_0^{[0]}(n;00)^\dagger\rangle$ and $\langle T_0^{[0]}(n;11)^\dagger\rangle$, and from (to) the $2p$ alignment multipoles $\langle T_q^{[2]}(n;11)^\dagger\rangle$. Further investigation shows that this limitation is actually a consequence of symmetry requirements on the collison system. We have written Eqs. (37d) and (39h) to emphasize these restrictions. Nevertheless, the mixed multipoles $\langle T_1^{[1]}(n;10)^\dagger\rangle$ of $2s-2p$ and the $2p$ orientation $\langle T_1^{[1]}(n;11)^\dagger\rangle$, can transfer each other, with the coefficients given by Eq. (36m). Since circular polarized light is related to the orientation of the excited states,[17] an obvious result of preceding arguments is that the decay radiation after the projectile goes away is not circular polarized unless the excited states at time $t=t_0$ are oriented or the density matrix connecting the $2s$ and $2p$ states is nonzero.

Alternatively, all multipoles are allowed to transfer to the $2p$ alignment states except the orientation multipole; as illustrated by Eqs. (38) and (39). Therefore we expect that the radiation may be linear polarized as long as the atom is not in the pure $2p$ orientation state at beginning. For instance, we could observe linear polarized light after collision even when the target is initially in the isotropic $2s$ state. We shall now investigate this process in more detail.

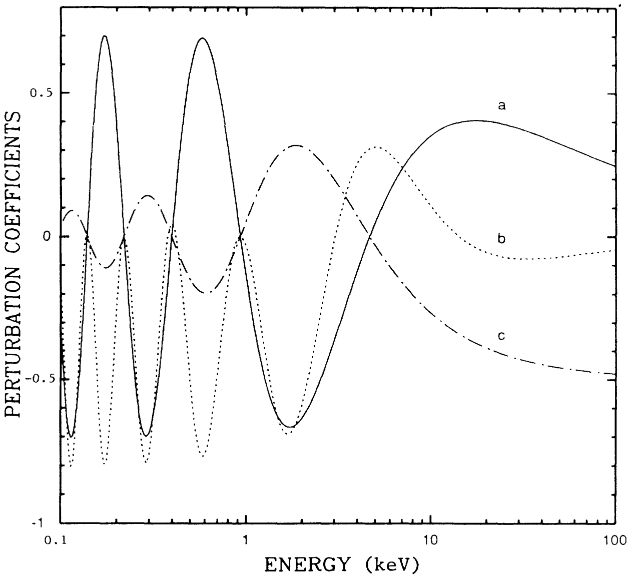

FIG. 2. Energy dependence of the perturbation coefficients: curve a, $G_n[(10)11t_0=1,(11)11t=+\infty]$; curve b, $G_n[(11)21t_0=0,\ (11)22t=+\infty]$; and curve c, $G_n[(00)00t_0=0,(11)20t=+\infty]$. The projectile is He$^+$. The impact parameter is $b=8$ a.u. In these and following figures, the logarithmic scale for the energy has been used because of the violent oscillation of the coefficients in the very-low-energy range.

Consider that the $2s$ state is initially excited, that is, $\langle T_0^{[0]}(n;00)^\dagger\rangle=1$, all other multipoles are zero at $t=-\infty$, and a proton goes by at a large impact parameter. The collision excites transitions from the $2s$ to the $2p$ state. This is basically a Born-type excitation for degenerate states. Evidently, all preceding formulas are valid except that we need to set the lower limit of integration in Eq. (19) to $-\infty$ so that Eq. (27) is replaced by $\omega=[1+(3/bv)^2]^{1/2}$, where we have used a straight-line trajectory approximation. The final-state multipoles are then determined by substituting the ω into Eqs. (24) and (25) and then into (36)–(38). The values of the resulting seven nonzero independent L multipoles versus incident energy are plotted in Fig. 3. Since

$$\mathrm{Tr}(\rho^2)=\sum_{k,q}\sum_{l'l}|\langle T_q^{[k]}(n;l'l)^\dagger\rangle|^2=1\ ,$$

we realize from these curves that the population is transferred from $|2s\rangle$ to $|2p\rangle$ partially or totally depending on the incident energy of the proton. It is somewhat surprising that at some energies, the isotropic $2s$ state is totally transferred into $2p$ state. At these energies, $\langle T_0^{[0]}(n;11)^\dagger\rangle=1$ and

$$\langle T_0^{[0]}(n;00)^\dagger=\langle T_1^{[1]}(n;11)^\dagger\rangle=\langle T_q^{[1]}(n;10)^\dagger\rangle=0\ .$$

The shape of the electron cloud is now completely described three alignment multipoles $\langle T_q^{[2]}(n;11)^\dagger\rangle$. It is also interesting that at some energies $\langle T_0^{[0]}(n;00)^\dagger\rangle$ takes its original value of unity and all other multipoles are zero. In other words, the hydrogen atom goes back to its original $2s$ state at the end of the collision, as if nothing happened. Of course, this is an integrated effect and by no means implies that there is no change in the states of the hydrogen during the collision process. We notice that $\langle T_0^{[0]}(n;00)^\dagger\rangle$ gradually approaches its limit value of unity as the incident energy increases. Thus the $2p$ charge cloud disappears in the high-energy ranges. In fact, there are almost no significant transfers at the energy of the order of a few hundred keV. This is what we expected since the magnetic-type interaction, which is the leading term at high energy, cannot induce the transition among the multipoles of different ranks.

The polarization

$$\begin{aligned}P&=(I_{\parallel}-I_{\perp})/(I_{\parallel}+I_{\perp})\\&=(1+\sqrt{3}\langle T_0^{[0]}(n;11)^\dagger\rangle/\langle T_2^{[2]}(n;11)^\dagger\rangle)^{-1}\ ,\end{aligned}$$

of the decay radiation is a measurable quantity, and provides a way to check present theory. The energy dependence of polarization after the proton goes by is depicted in Fig. 4. Note that here we have included the depolarization effect of the spin-orbit interaction. The fine structure cannot be ignored during the decay, although it can be ignored during the process of excitation and multipole conversion.[17,18]

Knowledge of the state multipoles amounts to the knowledge of charge cloud distributions. A direct application of our calculation is to make qualitative discussions on various features of the charge cloud by using obtained values of the state multipoles. For illustration, in the remainder of this section, let us find the symmetric axis of the $2p$ charge cloud after collision. This parameter has recently been emphasized in connection with alignment and orientation in collision excitation,[19,20] and is of physical significance.

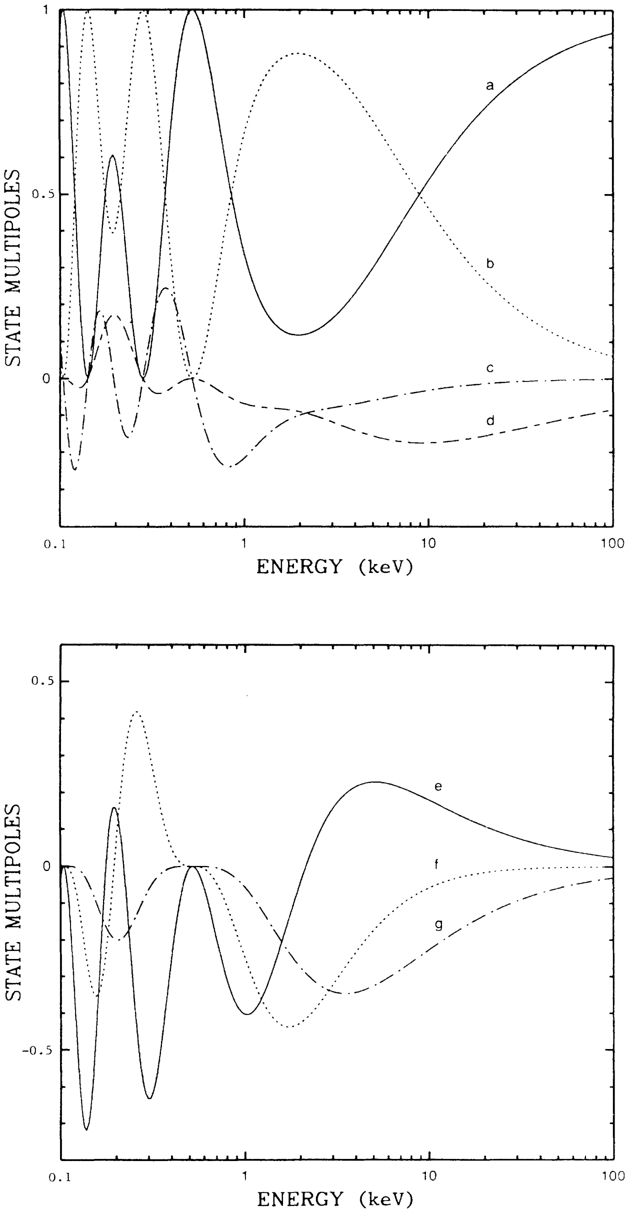

FIG. 3. Values of the state multipoles: curve a, $\langle T_0^{[0]}(n;00)^\dagger\rangle$; curve b, $\langle T_0^{[0]}(n;11)^\dagger\rangle$; curve c, $i^{-1}\langle T_0^{[1]}(n;\ 10)^\dagger\rangle$; curve d, $i^{-1}\langle T_1^{[1]}(n;10)^\dagger\rangle$; curve e, $\langle T_0^{[2]}(n;11)^\dagger\rangle$; curve f, $\langle T_1^{[2]}(n;11)^\dagger\rangle$; and curve g, $\langle T_2^{[2]}(n;11)^\dagger\rangle$ after the proton goes by in the energy ranges $0.1\sim100$ keV. The target hydrogen is supposed to be initially in the pure $2s$ state. The impact parameter is $b=12$ a.u.

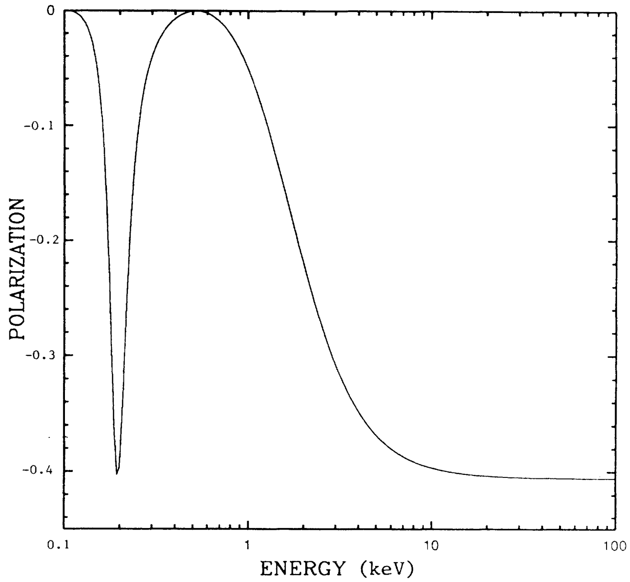

FIG. 4. Energy dependence of the polarization P in the energy range $0.1\sim100$ keV. The projectile is H^+ and the impact parameter is $b=12$ a.u.

The symmetric axis of the $2p$ charge cloud is the z' axis of a new frame in which the $\langle T_1^{[2]}(n;11)^+\rangle$ vanish.[21] This new frame can be obtained through a rotation about the y axis of the system. Considering the rotation property of the state multipoles, the angle ϕ between the z' at the z axis is found to be

$$\phi=\tfrac{1}{2}\tan^{-1}\frac{2\langle T_1^{[2]}(n;11)^\dagger\rangle}{\sqrt{3/2}\langle T_0^{[2]}(n;11)^\dagger\rangle-\langle T_2^{[2]}(n;11)^\dagger\rangle}\ . \tag{40}$$

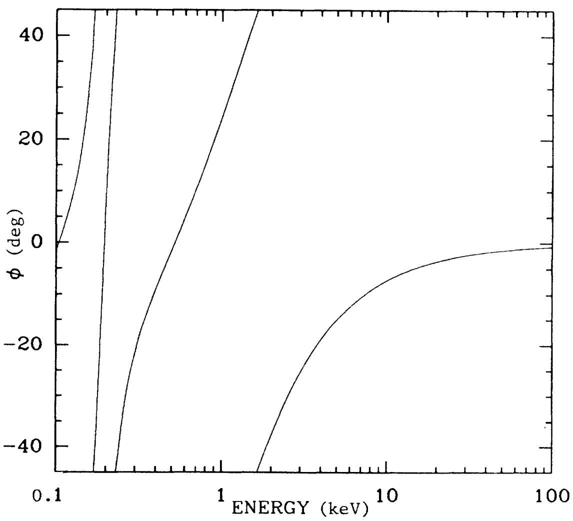

FIG. 5. Change of the angle between the direction of the symmetric axis of the $2p$ charge cloud and the beam direction as a function of the incident energy. The projectile is H^+ and the impact parameter is $b=12$ a.u.

This angle is also the angle between the direction of the symmetric axis of the $2p$ charge cloud and the incident direction of the beam as $t \rightarrow +\infty$ since the rotating frame xyz which we have been using coincides with the collision frame XYZ as time goes to infinity in the straight-line approximation. The changes of the angle ϕ versus the incident energy is plotted in the Fig. 5. It should be pointed out that there actually exist two symmetric axes for the $2p$ charge cloud which correspond to ϕ and $\phi+\pi/2$, respectively. These two axes plus the y axis of the system constitute three principal axes of the "ellipsoid of alignment."[21,22]

VI. SUMMARY

The calculation procedure used here is based on the orthogonal-operator expansion of the density operator and the choice of an appropriate orthogonal-operator set. Rather than attempting to obtain $G_n[(L'L)KQt_0,(l'l)kqt]$ for n excitation of hydrogen in the L representation, we first obtained the coefficients $G_j[(K_1K_2)KQt_0,(k_1,k_2)kqt]$, namely, Eq. (29), in the O(4) scheme. Our transformation formula (12) makes it possible to express $G_n[(L'L)KQt_0,(l'l)kqt]$ in terms of $G_j[(K_1K_2)KKQt_0,(k_1k_2)kqt]$ and to interpret the results in the L scheme.

The general formula (29) has been applied to $n=2$ excitation. Two salient features are worth emphasizing here. First, the isotropic $2s$ state can be totally or partially changed into $2p$ isotropic and alignment states under the influence of outgoing ion, and the transfers are more notable in the low-energy ranges. The transfer to a specific multipole from $2s$ monopole $\langle T_0^{[0]}(n;00)^\dagger\rangle$ has been found to oscillate with energy and can be over 50% at some energies. Second, the $2p$ orientation multipole $\langle T_1^{[1]}(n;11)^\dagger\rangle$ can be obtained only when the hydrogen is initially excited to the states which contain components of the first rank state multipoles $\langle T_q^{[1]}(n;L'L)^\dagger\rangle$. Transfers to this multipole from the monopole and alignment multipoles are forbidden.

Our discussion is presented in the context of the collision process with He^+ and H^+ projectiles, but the approach is clearly of great generality. Similar phenomena should also occur for other projectiles.

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