Adiabatic limit of inelastic transitions

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The widely used assumption that transitions induced by slowly changing perturbations are completely described by the topology of adiabatic energy surfaces in the plane of a complex perturbation parameter is reexamined. This assumption is the basis for the hidden crossings theory and most two-state models and yields an exponential decrease of transition probabilities and cross sections with decreasing speed of the perturbation v. We show that for a large class of problems, these approximations do not describe correctly transitions in the adiabatic limit. Contributions neglected lead, instead, to dominant power-law dependences in inelastic collisional cross sections, $\sigma \propto v^4$. We illustrate the interplay between different contributions for a collisional model system for which exact transition probabilities can be determined.

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Transitions between pairs of nearby energy levels of the same symmetry due to slowly varying perturbations have been the subject of intense investigations since the early days of quantum theory dating back to the seminal works of Born and Fock [1], Zwaan [2], Landau [3], Zener [4], and Stueckelberg [5]. Nonadiabatic transitions are introduced by allowing the parameter $R(t)$ and, hence, the Hamiltonian $H(R)$ to become slowly time dependent. The key parameter that controls the adiabaticity of the process is the speed of the parametric deformation, $v_R = |dR(t)/dt|$. For an atomic collision, R is the internuclear distance and in the limit $R \to \infty$, v_R tends to the collision velocity, v. Born and Fock showed that transition probabilities should become exceedingly small when the Hamiltonian varies slowly in time (nowadays referred to as the adiabatic theorem) and provided upper bounds for transition rates as a function of v_R. Subsequently, Landau arrived at the more quantitative conclusion that transition probabilities for analytic Hamiltonians should decrease exponentially as $\exp(-\text{const}/v_R)$.

The paradigm for nonadiabatic transitions is the celebrated Landau-Zener (LZ) ''curve crossing'' model [3,4,6] which has found widespread applications in many areas of physics and chemistry. It assumes the crossing of a pair of diabatic energy levels at some value $R = R_c$ and a constant diabatic coupling in its vicinity. In the adiabatic representation this maps onto an avoided crossing at R_c of a pair of adiabatic energy levels, $E_f(R)$ and $E_i(R)$ of the adiabatic Hamiltonian $H(R)$, while the coupling assumes the form of a Lorentzian peaked at R_c. Although $E_i(R)$ and $E_f(R)$ cannot cross for real values of R, their continuation into the complex R plane do cross (bars denote complex variables) where the Hamiltonian $H(R)$ is not Hermitian [2]. The splitting $\Delta E_{fi}(R) = E_f(R) - E_i(R)$ has zeroes at $R = R_c$ of the form of square-root branch points. These branch points define the avoided crossings of E_f and E_i at $R_c = \mathrm{Re}\{R_c\}$ and the local maxima of the nonadiabatic coupling between a pair of adiabatic states. The LZ transition around R_c can be fully described in terms of R_c and $\Delta E_{f,i}(R_c) = E_f(R_c) - E_i(R_c)$. Other examples for models of transitions induced by slowly varying interactions are those involving parallel quasiresonant diabatic states where the coupling between them is assumed to be an exponential function of R [7,8]. These also can be expressed in terms of the parameters of the complex adiabatic energy surface [9,10].

Common to all these models of nonadiabatic transitions is the assumption that the topology of the adiabatic energies determines the dynamics of the system in the adiabatic limit. Transitions between energy levels are exclusively associated with branch points of the energy surface and any other contributions are assumed to be negligible. A general approach that exploits these ideas is known as the hidden crossings (HC) or advanced adiabatic theory [11,10,12,13]. Although the basic principles were proposed by Zwaan [2], Stueckelberg [5], and Landau [3,6], Solov'ev [11,10] elevated them to the level of a unified theory, applicable to slow heavy-particle collisions and other slow phenomena. This is achieved by three steps: (1) Defining a Hamiltonian in coordinates in which the nuclei are at rest such that the adiabatic eigenfunctions have the correct asymptotic behavior for $R \to \infty$. (2) Extensively studying the topology of the unique, multivalued adiabatic energy surface in the plane of complex R, whose various Riemann sheets for real R yield all adiabatic energy levels. (3) Constructing the S matrix which accounts for the R-localized two-state transitions defined by the branch points found in (2) and the adiabatic evolution between the regions of localization along all possible transition paths which connect intial and final states [12–15]. Numerous studies have revealed various series of branch points which connect the adiabatic energy branches in a pairwise fashion. The best known are the Q series, associated with the top of the radial potential barrier between the colliding centers, and the S series, associated with the centrifugal barrier in the united atom limit. In the former, when a level crosses the R-changing top of the barrier, the electronic wave function changes its character from an atomic to a molecular one (or vice versa). This sudden change with R induces a transition since it leads to a local maximum of the nonadiabatic coupling

$$U_{f,i}(R)=\left\langle \phi_f(R)\left|\frac{d}{dR}\right|\phi_i(R)\right\rangle, \tag{1}$$

where $H(R)|\phi_{i,f}(R)\rangle=E_{i,f}(R)|\phi_{i,f}(R)\rangle$. The maximum of the coupling is a projection of a pole of $U_{f,i}(R)$ at $\bar{R}_c$ such that in its vicinity [10,16]

$$U_{f,i}(R)\simeq U_{f,i}^{\mathrm{HC}}(R)=\frac{1}{2}\frac{\mathrm{Im}\{\bar{R}_c\}}{(R-\mathrm{Re}\{\bar{R}_c\})^2+(\mathrm{Im}\{\bar{R}_c\})^2}. \tag{2}$$

Most models of nonadiabatic transitions can be related to the topology of adiabatic energy surfaces. The *Q*-type hidden crossings correspond to the Landau-Zener model, the Demkov model is described by the *P*-type hidden crossings, while the *S*-type hidden crossings are sometimes associated with the Fano-Lichten promotion mechanism [17]. These types of hidden crossings always appear as promotional series. In addition, an isolated Landau-Zener narrow crossing corresponds to the case in which two adiabatic levels accidentally become almost degenerate close to the top of the potential barrier and is characterized by a branch point very close to the real-R axis which does not belong to any series [10] and describes tunneling through the barrier.

As a consequence of the HC theory, transition probabilities and cross sections are exponentially decreasing functions of $1/v$, i.e., $\sim\exp(-\mathrm{const}/v)$ [10]. In this paper we challenge the hypothesis that such a trend should continue in general at low velocities and, in particular, when $v\to 0$. We show that for a large class of slowly varying time-dependent quantum systems the adiabatic limit rather emerges from the ''topology'' of the radial velocity in the vicinity of the classical turning point. We find that the dominant contribution at low velocities gives rise to a power-law behavior of collisional cross sections ($\sigma_{i,f}\propto v_R^n$) instead of an exponential. This behavior is not related to other power-law dependences of collisional cross sections, which are expected at very low collision energies, due to trajectory acceleration [18] or near threshold [19]. To be specific, we employ in the following as the time-dependent parameter $R(t)$ the internuclear distance in the form $R(t)=\sqrt{b^2+(vt)^2}$ for slow atomic collisions in the impact parameter, b, approximation [20], thus employing straight-line trajectories with constant speed v. The electronic motion is described by the adiabatic electronic Hamiltonian $H(R)$ of such a collision system. We emphasize, however, that our basic findings are independent of the model system chosen and applicable to a wide range of physical systems including chemical reactions, molecular dissociations, and interactions of atoms with slowly varying fields.

Our point of departure is the first-order adiabatic perturbation theory [1] within which the transition amplitude (or *S*-matrix element) is given by

$$S_{f,i}=-\int_{-\infty}^{\infty}dt\frac{dR}{dt}U_{f,i}[R(t)]\exp\left[i\int_0^t dt'\Delta E_{f,i}(R(t'))\right], \tag{3}$$

where we assume in the following, for definiteness, $\Delta E_{f,i}(R(t))>0$. In the present case, $v_R=v^2t/\sqrt{b^2+(vt)^2}$.

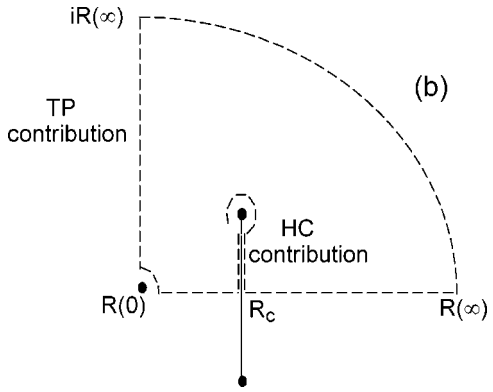

FIG. 1. (a) Schematic diagram of the incomplete passage through an avoided crossing. (b) Proper integration contour (dashed line) to evaluate the *S*-matrix [Eq. (4)] illustrating the origin of the TP and HC contributions. The black dots indicate the branch points of the radial velocity near $R(0)$ and of the nonadiabatic matrix element near R_c (the vertical line indicates the branch cut). The loops around these points are infinitesimally narrow.

The key point is that $R(t)$ is not a monotonic function of t but $v_R(t)$ reverses its sign at the turning point (TP) at $t=0$ and $R(0)$. In terms of the parameter R, the *S*-matrix element becomes, up to an overall phase,

$$S_{f,i}=-2i\,\mathrm{Im}\left\{\int_{R(0)}^{R(\infty)}dR\,U_{f,i}(R)\times\exp\left[i\int_{R(0)}^{R}\frac{\Delta E_{f,i}(R')}{|v_{R'}|}dR'\right]\right\}. \tag{4}$$

If one now assumes that $U_{f,i}(R)$ vanishes at both integration limits $R(0)$ and $R(\infty)$ in Eq. (4) and along a loop in the complex R plane (Fig. 1) the R integral gives only a contribution due to a branch point at $\bar{R}_c$. Thus closing the contour integral in the upper half plane and isolating the contribution from the branch point gives the perturbation theory limit of the standard hidden crossings result [14,16]

$$S_{f,i}\simeq S_{f,i}^{\mathrm{HC}}=-2i\exp[-|\mathrm{Im}\{F_{f,i}(\bar{R}_c)\}|]\sin[\mathrm{Re}\{F_{f,i}(\bar{R}_c)\}], \tag{5}$$

where

$$F_{f,i}(\bar{R}_c)=\int_{\mathcal{C}}dR\frac{\Delta E_{f,i}(R)}{|v_{R'}|} \tag{6}$$

and the contour $\mathcal{C}$ starts at $R=R(0)$, continues on the real axis up to $R=R_c-\epsilon$, encircles R_c and ends at $R=R_c+\epsilon$, $\epsilon>0$ being infinitesimally small. The oscillation-averaged HC transition probability, $|S_{f,i}|^2\propto\exp[-2|\mathrm{Im}\{F_{f,i}(\bar{R}_c)\}|]$, decays exponentially with $v^{-1}(\sim v_R^{-1})$ as $v\to 0$. This velocity dependence obviously results from taking the limit $U_{f,i}(R(0))/\Delta E_{f,i}(R(0))\to 0$ in the evaluation of Eq. (4) prior to the limit $v_R\to 0$.

For any finite value of the coupling at the TP, $U_{f,i}(R(0)) \neq 0$, closing the contour of integration is more involved. There exists an additional contribution to the transition amplitude due to the integral from $\bar{R}=R(0)$ to $\underline{R}=R(0)+iR(\infty)$ along the line parallel to the imaginary R axis in Fig. 1. Thus proper contour integration [21], including this line, leads to an additional TP contribution to the S-matrix element,

$$S_{f,i}=S_{f,i}^{\mathrm{HC}}+S_{f,i}^{\mathrm{TP}}, \tag{7}$$

where $S_{f,i}^{\mathrm{TP}}$ is obtained replacing $R(\infty)$ by $\bar{R}=R(0)+iR(\infty)$ in Eq. (4). Expanding this integral for small impact parameters $b<|\Delta E_{f,i}(0)/v|$ and in the limit of low velocities $|v/\Delta E_{f,i}(0)| \ll 1$,

$$S_{f,i}^{\mathrm{TP}} \simeq -2ibU_{f,i}(0)K_1\left(\frac{\Delta E_{f,i}(0)}{v}b\right), \tag{8}$$

where K_1 is a modified Bessel function and the argument ''0'' designates $R=0$. The effect, described by Eq. (8) maximizes for b=0, yielding $S_{f,i}^{\mathrm{TP}} \sim v/\Delta E_{f,i}(0)$. It is instructive to note that the same result for $S_{f,i}^{\mathrm{TP}}$ can be obtained when the integration is performed in Eq. (3) rather than in Eq. (4), over a contour in the complex time domain [21]. In this case, the TP result in Eq. (8) is associated with a contribution of the square root branch points of the radial velocity at the turning point, which is located at $v\bar{t}_c=\pm ib$. The deformation of the contour in Fig. 1 near $R(0)$ avoids the branch point of the radial velocity v_R. The existence of this branch point has been recognized by several authors [18,22,23], but its contribution to the integral in Eq. (4) was neglected or only partially taken into account [24], in the phase for $b=0$. The TP branch point at $R=R(0)$ is real (unlike $\bar{R}_c$), which explains its dominant influence when $v \to 0$.

Transitions near the turning point take place effectively only inside the adiabatic cut-off radius b defined by

$$\frac{\Delta E_{f,i}(0)\, b}{v} \lesssim 1, \tag{9}$$

i.e., when the characteristic frequency $\omega \approx v/b$ of $R(t)$ is at least of the order of the energy gap between the energy levels near the turning point. The total cross section due to the TP contribution follows from Eq. (8) as

$$\sigma_{f,i}^{\mathrm{TP}}=\int_0^\infty dbb|S_{f,i}^{\mathrm{TP}}(b)|^2=\frac{64}{3}\pi\left|\frac{U_{f,i}(0)}{\Delta E_{f,i}(0)}\right|^2\left(\frac{\frac{1}{2}v^2}{\Delta E_{f,i}(0)}\right)^2, \tag{10}$$

where $U_{fi}(0)$ is the exact value of the nonadiabatic matrix element, Eq. (1). Remarkably, this contribution increases with the fourth power of v, or equivalently, with the square of the translational kinetic energy of the electron in units of the energy gap at $R=0$. Its size is controlled by the ratio of the nonadiabatic coupling to the energy splitting at $R=0$. As $v \to 0$, this term, unlike the exponentially suppressed HC contribution, gives the dominant adiabatic limit for the inelastic cross section. Note that Eqs. (8) and (10) are valid irrespective of the particular form of either the adiabatic coupling matrix element, $U_{f,i}(R)$, or the adiabatic energies, $E_{f,i}(R)$. Being defined only by quantities at $R=0$, it gives the leading contribution to the ''radial'' transition probability irrespective of the existence of a hidden crossing between the terms i and f (i.e., even if $S_{f,i}^{\mathrm{HC}}=0$). This may be of particular importance because it is a mechanism for direct excitation between two distant energy levels. If $U_{fi}(0)=0$, much like for homonuclear ion-atom collisions, higher-order contributions proportional to $d^2U_{fi}(R)/dR^2|_{R=0}$ need to be taken into account, yielding a cross section dependence proportional to v^8.

It may appear that Eq. (4) is a peculiarity due to the time dependence of ion-atom collisions in the impact parameter method. This is, however, not the case. Incomplete passage through avoided crossings is, in fact, generic. Examples include the ramping up and down of an external field $F(t)$ from $F(-\infty)=0$ to $F_{\max}=F(0)$ and back to $F(\infty)=0$ featuring an effective turning point at $F(0)$, where the two levels mixed by the field are usually not decoupled. Thus the TP effect is always present for an atom subject to a slow time-dependent electric field. For example, a direct application of the present results can be performed for a half-cycle laser pulse with an electric field envelope defined by $F=\sqrt{a^2+\gamma^2t^2}-\sqrt{a^2/2+\gamma^2t^2}$, where a and γ are control parameters. Likewise, photodissociation starting at an equilibrium distance of the molecular constituents and approaching infinity, may feature the incomplete passage through one (or several) avoided crossing(s) on the outbound trajectory.

We have verified the significance of the TP transition to nonadiabatic processes for a simple one-dimensional (1D) model of a collision system in which the target and the projectile are represented by harmonic wells,

$$H(R)=\frac{p^2}{2}+\frac{1}{2}\left(|x|-\frac{R}{2}\right)^2, \tag{11}$$

where x and p are the position and momentum of the electron with respect to the center of mass of the collision system. ''Molecular'' eigenstates, $|\phi_n(R)\rangle$, and energy levels, $E_n(R)$, of this system can be found in quantum mechanics textbooks (see, e.g., [25]). In the limit $R \to 0$, the system becomes a single harmonic oscillator with $E_n \to (n+0.5)$. In turn, for $R \to \infty$ the system develops into two well-separated harmonic wells with $E_n \to ([n/2]+0.5)$, where [ ] denotes the integer part. This system features only Q-type hidden crossings, which significantly simplifies the nonadiabatic dynamics. The advantage of studying this simple collision system is that exact transition probabilities can be easily obtained by numerically solving the time-dependent Schrödinger equation (TDSE). Moreover, since turning-point effects could potentially be contaminated by the breakdown of the classical trajectory description underlying the impact-parameter method, we have embedded the model Hamiltonian, Eq. (11), into a 3D model, in which the internuclear motion is described quantum mechanically [26,27]. This quantum coupling (QC) problem can be solved exactly as well. Artifacts

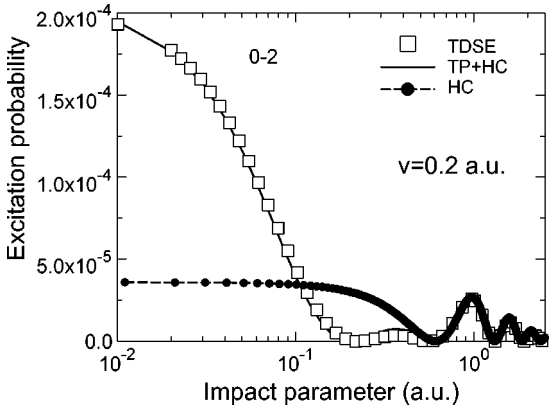

FIG. 2. Excitation probability from $n=0$ onto $n=2$ for $v=0.2$ as a function of the impact parameter. The HC contribution to the transition probability is negligible for small impact parameters but it dominates for $b>v/\Delta E_{21}(0)\sim 0.1$ a.u. In the transition region, TP+HC calculations can be smaller than the HC calculations because of the destructive interference between the TP and HC amplitudes.

due to the classical description of the trajectory near the turning point are therefore ruled out.

The TDSE transition probability as a function of the impact parameter b at a fixed velocity $v=0.2$ (Fig. 2), is perfectly reproduced by the S-matrix including both the HC and TP contributions [Eq. (7)]. For comparison, the standard HC result is also shown. Obviously, at large impact parameters outside the adiabatic cutoff for turning-point contributions [Eq. (9)], the HC approximation works well. Inside the adiabatic radius, the TP contribution dominates and the HC approximation breaks down. Likewise, the total cross section $\sigma_{f,i}$ [Fig. 3(a)], as a function of the inverse collision velocity, agrees very well with the TSDE result. Furthermore, the QC calculation for a typical reduced mass of $\mu=1$ amu also agrees extremely well with the low-velocity S-matrix including TP contributions. The crucial point to be noted is that the standard HC approximation leads to large discrepancies for small v due to its exponential decay with $1/v$, while the correct adiabatic limit features a power law ($\approx v^4$). The TP effect is significant here already at about $v=0.2$ a.u. or a center-of-mass collision energy of about 1 keV/amu in the QC calculation. Since transitions near the TP in realistic collisions can be influenced by the interaction potential between the heavy nuclei, we have investigated the effect of the internuclear interaction on the transition probabilities within the QC approach by incorporating a potential $V_{\rm nuc}(R)=\pm\exp(-2R)/R$, where the sign of the potential determines whether the interaction is attractive or repulsive. Figure 3(b) compares the results of such calculations with the one obtained for $V_{\rm nuc}(R)=0$. As is intuitively expected, an attractive (repulsive) potential increases (decreases) the value of the cross section. The point to be noted, however, is that both calculations for an attractive or a repulsive potential differ from the HC predictions and the differences are, once again, due to the TP contribution. Finally, we note that the small values of the cross sections in Fig. 3 and the probabilities in Fig. 2 originate in the particular parameters used for the

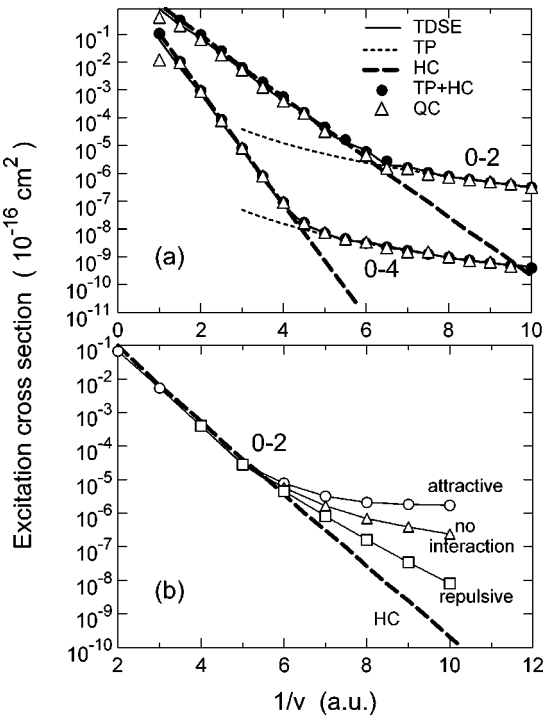

FIG. 3. The cross sections for excitation from $n=0$ onto $n=2$ and $n=4$ as a function of the inverse velocity. (a) HC calculations are quite accurate for $v_n<v<1$, where $v_2=0.15$ and $v_4=0.25$. For $v_n>v$, HC greatly underestimates the cross section which is predominantly given by the TP contribution. Coherent combination of the HC and TP amplitudes leads to complete agreement with exact TDSE and QC cross sections. For $v<v_4$, the excitation cross section from $n=0$ to $n=4$ is determined by the TP contribution, defined by the direct coupling between $n=0$ and $n=4$ states at $R=0$. At larger velocities, this excitation process is governed by sequential $0-2$ and $2-4$ HC transitions, since there is no branch point directly connecting the levels $n=0$ and $n=4$. (b) The HC result is compared with QC calculations involving different internuclear interactions: attractive $V_{\rm nuc}(R)=-\exp(-2R)/R$, repulsive $V_{\rm nuc}(R)=\exp(-2R)/R$, and no interaction.

double-harmonic oscillator model: i.e., a frequency of the oscillator of the order of 1 yields both imaginary parts of the hidden crossings and energy splitting at $R=0$ of the order of 1 and, thus, small HC and TP contributions in the limit of small velocities.

In summary, we have shown that the low velocity dependence of inelastic transition cross sections is, in general, not exponential in the adiabatic limit, as suggested by the hidden crossings theory and other models of nonadiabatic couplings, including those that include effects of turning point through trajectory acceleration effects [18]. Instead, the adiabatic limit is controlled by the ratio of the adiabatic coupling to the energy gap between energy levels near the turning point of the perturbation. Whenever turning points exist within the ''adiabatic radius,'' Eq. (9), and this ratio at the turning point is nonzero, deviations from the exponential velocity dependence are to be expected. This result holds irrespective of the detailed properties of the curve-crossing systems under consideration. In the case of ion-atom collisions, cross sections

were found here to display a power-law dependence on the collision velocity. Work is under way to unambiguously identify TP effects in inelastic transitions in realistic systems under a slow time-dependent perturbation.

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[1] M. Born and V. Fock, Z. Phys. **51**, 165 (1928).
[2] A. Zwaan, Arch. Nederland IIIA **12**, 1 (1929).
[3] L. D. Landau, Phys. Z. Sowjetunion **2**, 46 (1932).
[4] C. Zener, Proc. R. Soc. London, Ser. A **137**, 696 (1932).
[5] E. C. G. Stueckelberg, Helv. Phys. Acta **5**, 369 (1932).
[6] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-Relativistic Theory)* (Pergamon, New York, 1965).
[7] Yu. N. Demkov, Zh. Éksp. Teor. Fiz. **45**, 159 (1963) [Sov. Phys. JETP **18**, 138 (1964)].
[8] W. Rosen and C. Zener, Phys. Rev. **40**, 502 (1932).
[9] R. K. Janev, J. Phys. B **30**, 2019 (1997).
[10] E. A. Solov'ev, Usp. Fiz. Nauk **157**, 438 (1989) [Sov. Phys. Usp. **32**, 228 (1989)] and references therein.
[11] W. A. Solov'ev, Zh. Éksp. Teor. Fiz. **81**, 1681 (1981) [Sov. Phys. JETP **54**, 893 (1981)].
[12] T. P. Grozdanov and E. A. Solov'ev, Phys. Rev. A **44**, 5605 (1990).
[13] P. S. Krstić and R. K. Janev, Phys. Rev. A **47**, 3894 (1993); P. S. Krstić *et al.*, J. Phys. B **29**, 1941 (1996).
[14] R. K. Janev *et al.*, J. Phys. B **30**, L353 (1998).
[15] P. S. Krstić *et al.*, Phys. Rev. Lett. (to be published).
[16] P. S. Krstić *et al.*, J. Phys. B **31**, L155 (1998).
[17] U. Fano and W. Lichten, Phys. Rev. Lett. **14**, 627 (1965).
[18] E. E. Nikitin and S. Ya. Umanskii, *Theory of Slow Atomic Collisions* (Springer, Berlin, 1984), Vol. 30, Chap. 8, and references therein.
[19] G. H. Wannier, Phys. Rev. **90**, 817 (1953).
[20] B. H. Brandsen and M. R. C. McDowell, *Charge Exchange and the Theory of Ion-Atom Collisions* (Clarendon, Oxford, 1992).
[21] P. S. Krstić, C. O. Reinhold, and J. Burgdörfer, Phys. Rev. A (to be published).
[22] M. S. Child, *Semiclassical Mechanics with Molecular Applications* (Claredon, Oxford, 1998), and references therein.
[23] V. N. Ostrovsky, Phys. Rev. A **61**, 032505 (2000).
[24] R. K. Janev, L. P. Presnyakov, and V. P. Shevelko, *Physics of Highly Charged Ions* (Springer-Verlag, New York, 1985).
[25] E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1970).
[26] T. G. Heil *et al.*, Phys. Rev. A **23**, 1100 (1981).
[27] B. R. Johnson, J. Comput. Phys. **13**, 445 (1973).