Retardation Effects and the Born-Oppenheimer Approximation: Theory of Tunneling Ionization of Molecules Revisited

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We show that retardation in adjusting an electronic state to an instantaneous internuclear configuration caused by the finiteness of the electron's velocity breaks the validity of the Born-Oppenheimer (BO) approximation at large electron-nuclei distances. This applies even to the ground state. As a result, the BO approximation in the theory of tunneling ionization of molecules breaks down at sufficiently weak fields. We also show that to account for nuclear motion the weak-field asymptotic expansion for the tunneling ionization rate must be restructured. The predictions for the rate using the BO approximation and the asymptotic expansion are compared with numerical results for a one-dimensional three-body system modeling a diatomic molecule, with both electronic and nuclear motions treated exactly.

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Tunneling ionization in a static electric field is one of the fundamental problems of quantum mechanics. In recent years this problem has attracted a new wave of interest motivated by its applications in strong-field and attosecond physics [1]. The theory of tunneling ionization was pioneered by Oppenheimer [2] who showed that the ionization rate Γ in a field F is proportional to $\exp[-2(2I_p)^{3/2}/3F]$, where I_p is the ionization potential of the system (atomic units $\hbar = m_e = |e| = 1$ are used throughout). The exponent here has a classical origin and is twice the action accumulated by an electron on its way to the outer turning point, provided the field is sufficiently weak and the turning point lies far away from the unperturbed system. It took three decades before the correct preexponential factor in the dependence of Γ on F was obtained for the hydrogen atom in the ground state [3]. This result was soon generalized to ionization from an arbitrary state in a spherically symmetric potential [4]. Subsequent studies of the Coulomb potential [5–8], for which the problem allows a detailed analysis due to separability of variables in parabolic coordinates, revealed the asymptotic nature of these results. In the tunneling regime $\ln\Gamma$ can be obtained as an asymptotic expansion in F, with Oppenheimer's exponent giving the leading-order $[O(F^{-1})]$ term. The next two terms $[O(\ln F)$ and $O(F^0)]$ are determined by the asymptotic tail of the unperturbed wave function, so tunneling ionization is said to probe the tail. Further development of this approach culminated in the weak-field asymptotic theory (WFAT) [9,10] which extended the results of Refs. [3,5–8] to arbitrary potentials without any symmetry. A recent generalization of the WFAT to multielectron systems in the frozen-nuclei approximation [11] shows that in this case the many-body character of the problem does not qualitatively change the asymptotic expansion for $\ln\Gamma$, because the energy spacing between electronic states of the parent ion is normally of the same order as the ionization potential.

Rovibrational states of molecules, on the other hand, have a much denser spectrum. One therefore can expect that the structure of the asymptotic expansion for the ionization rate of molecules with nuclear motion taken into account may differ from that for frozen nuclei. The Born-Oppenheimer (BO) approximation seems to suggest a natural framework for incorporating nuclear motion into the theory [12–14]. However, it is not evident whether this approximation holds in the tunneling problem. This can be seen already from the fact that in the BO approximation the energy required to detach an electron continuously depends on the internuclear configuration. Is it this energy, e.g., in the equilibrium configuration of a neutral molecule, or the true ionization potential corresponding to a relaxed configuration of the molecular ion that defines Oppenheimer's exponent in this case? In this Letter, we show that there exists a general physical mechanism—retardation in adjusting the electronic state to an instantaneous internuclear configuration—that breaks the validity of the BO approximation at large electron-nuclei distances, and this has important consequences for the theory of tunneling ionization of molecules. This mechanism is related, of course, to other well-known manifestations of the breakdown of the BO approximation, e.g., at avoided crossings [15] and conical intersections [16] of electronic states and in Rydberg states [17].

Accurate calculation of tunneling ionization rates of molecules in a static electric field is a challenging computational task. We are aware of only a few such calculations for one- [18–22] and two-electron [12] diatomic molecules with frozen nuclei. The extension of such calculations to a full quantum-mechanical treatment of nuclear motion in the three-dimensional case is prohibitively difficult.

We therefore consider a one-dimensional three-body system consisting of two identical heavy particles (nuclei) with masses $M \gg 1$ and charges $+0.5$ and an electron with mass 1 and charge -1. Let x_1, x_2, and x_3 be the coordinates of the particles in the inertial center-of-mass frame, $M(x_1 + x_2) + x_3 = 0$. The Schrödinger equation for the system reads

$$\left[-\frac{1}{M}\frac{d^2}{dR^2} - \frac{1}{2m}\frac{d^2}{dx^2} + U(R) + V(x;R) + Fx - E(F)\right] \times \Psi(x,R) = 0, \tag{1}$$

where $R = x_2 - x_1$ and $x = x_3/m$ are the Jacobi coordinates and $m = 2M/(2M+1)$ is the reduced mass of the electron. The heavy subsystem models a diatomic molecular ion. Our goal is to analyze the effect of nuclear motion on tunneling ionization of an electron. To focus on the electron tunneling, here we exclude the dissociation channel from consideration. To this end, the internuclear interaction is modeled by the potential

$$U(R) = \frac{A}{R^2} + B + CR^2, \tag{2}$$

which has a purely discrete spectrum. The coefficients $A = 0.26$, $B = -0.732\,635$, and $C = 0.016\,25$ are chosen to reproduce the BO potential in H_2^+ (Fig. 1). The electron-nuclear interaction is described by

$$V(x;R) = V(x + R/2) + V(x - R/2), \tag{3a}$$

$$V(x) = \frac{-a}{\cosh^2(bx)}. \tag{3b}$$

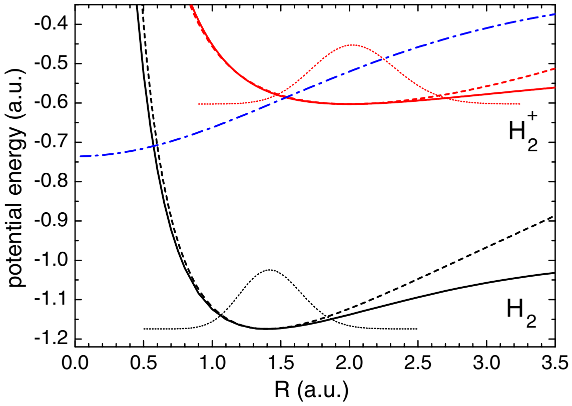

FIG. 1 (color online). Solid lines: BO potentials for the ground electronic states of H_2^+ [23] and H_2 [24] as functions of the internuclear distance R. Dashed lines: present model internuclear potential $U(R)$ (upper) and BO potential for the three-body system $U(R) + E_e(R,0)$ (lower). Dashed-dotted line: present electronic energy $E_e(R,0)$. Dotted lines: lowest internuclear $\phi_0(R)$ [upper, Eq. (6)] and BO $\chi(R)$ [lower, Eq. (5)] vibrational states for $M = m_p$.

The only reason to use a finite-range potential (3b) is to simplify the following equations. The BO approximation corresponds to $M \to \infty$. In this limit $m = 1$ and the solution to Eq. (1) takes the form $\Psi_{BO}(x,R) = \psi_e(x;R)\chi(R)$, where the electronic and nuclear wave functions satisfy

$$\left[-\frac{1}{2}\frac{d^2}{dx^2} + V(x;R) + Fx - E_e(R,F)\right]\psi_e(x;R) = 0 \tag{4}$$

and

$$\left[-\frac{1}{M}\frac{d^2}{dR^2} + U(R) + E_e(R,F) - E_{BO}(F)\right]\chi(R) = 0. \tag{5}$$

With the coefficients $a = 0.62772$ and $b = 0.857$ in Eq. (3b), the potential in Eq. (5) for $F = 0$ reproduces the BO potential in H_2 (Fig. 1). We solve these equations subject to zero boundary conditions $\Psi(x,0) = \Psi(x,\infty) = 0$ in R and outgoing-wave boundary conditions in x. This is an eigenvalue problem, so the energies $E(F)$, $E_e(R,F)$, and $E_{BO}(F)$ depend on field F. It should be noted that, in spite of all the simplifications in our model, Eq. (1) treats both electronic and nuclear motions without any approximations, and this is essential for uncovering important aspects of tunneling ionization dynamics in molecules.

We first discuss the ground state of the molecule in the field-free case, $F = 0$. To solve Eq. (1), we introduce a complete set of vibrational states of the molecular ion:

$$\left[-\frac{1}{M}\frac{d^2}{dR^2} + U(R) - \varepsilon_v\right]\phi_v(R) = 0, \qquad v = 0, 1, \ldots. \tag{6}$$

The solution to Eq. (1) is sought in the form

$$\Psi(x,R) = \sum_v f_v(x)\phi_v(R). \tag{7}$$

Substituting this expansion into Eq. (1), we obtain a set of coupled equations for $f_v(x)$ which are solved by the slow variable discretization (SVD) method [25]. The functions $f_v(x)$ satisfy

$$f_v(x)|_{|x|\to\infty} = g_v e^{-\varkappa_v|x|}, \qquad \varkappa_v = \sqrt{2m[\varepsilon_v - E(0)]}, \tag{8}$$

where $E(0)$ is the ground-state energy. We wish to compare the exact wave function with the BO approximation at large electron-nuclei distances, that is, large x. To do this, let us introduce the electron density:

$$\rho(x) = \int_0^\infty \Psi^2(x,R)dR. \tag{9}$$

For the present model, $\rho(x) = \rho(-x)$. The behavior of $\rho(x)$ is shown in Fig. 2. To facilitate comparison of the exact and BO results, $\rho(x)$ is multiplied by $e^{2\varkappa_0 x}$, which compensates the exponential factor in Eq. (8) for the lowest vibrational channel; without this factor, $\rho(x)$ rapidly decays as x grows. From Eqs. (7) and (8) we have $\rho(x \to \infty) = \sum_v g_v^2 e^{-2\varkappa_v x} \to g_0^2 e^{-2\varkappa_0 x}$, so the product $e^{2\varkappa_0 x}\rho(x)$ should monotonically decay and approach a constant g_0^2 at $x \to \infty$. This is the case for the exact results, but not for the BO approximation. To emphasize the difference, we show the results for three values of the nuclear mass M equal to fractions of the proton mass $m_p = 1836$. For $M = m_p$, the error of the BO results is less dramatic in the interval of x considered, but still reaches 10% at $x = 25$. We stress that the BO approximation works well for the energy of the system. Indeed, $E(0)$ and $E_{\mathrm{BO}}(0)$ differ only by 0.03% for $M = 250$, and the difference decays $\propto 1/M$ as M grows. It works well also for the wave function in the region of its localization. But it breaks down in the asymptotic region $x \to \infty$, and this is the first of our findings.

To clarify the physical mechanism responsible for the breakdown of the BO approximation at large electron-nuclei distances, we consider a time-dependent problem associated with Eq. (1). Let us temporarily treat the nuclei classically, and let $R(t)$ be the internuclear distance describing their vibrational motion. Using the retarded Green function [26], the time-dependent Schrödinger equation for the electronic wave function $\psi(x, t)$ can be presented in the integral form

$$\psi(x,t) = -e^{i\pi/4}\int dx' \int_{-\infty}^{t} V(x'; R(t'))\,\psi(x',t')\frac{e^{iS(t')}dt'}{\sqrt{2\pi\delta t}}, \tag{10}$$

where $S(t')$ is the classical action

$$S(t') = \frac{(x-x')^2}{2\delta t} - \frac{1}{2}F(x+x')\delta t - \frac{1}{24}F^2\delta t^3, \tag{11}$$

and $\delta t = t - t'$. Let T be the time during which $R(t)$ changes appreciably. It can be estimated by $T = 1/2\omega_e$, where the frequency ω_e is defined by the expansion $U(R) + E_e(R,0) \approx U(R_0) + E_e(R_0,0) + \frac{1}{4}M\omega_e^2(R-R_0)^2$ and $R_0 = 1.4$ is the equilibrium internuclear distance (Fig. 1). Note that $\omega_e \propto M^{-1/2}$, and hence $T \propto M^{1/2}$; thus, T grows with M. The BO approximation for Eq. (1) amounts to the adiabatic approximation for Eq. (10). The asymptotic solution of Eq. (10) for $T \to \infty$ can be obtained using the procedure developed in Ref. [27] and is given by $\psi(x,t) = \psi_e(x; R(t))\exp[-i\int^t E_e(R(t'),F)dt']$, where $E_e(R,F)$ and $\psi_e(x;R)$ are defined by Eq. (4). The derivation is based on evaluating the time integral in Eq. (10) by the steepest descent method, with the saddle points t'_{SP} defined by $\partial S(t')/\partial t' = E_e(R(t'),F)$. The condition of validity of the adiabatic approximation is $|t'_{\mathrm{SP}} - t| \ll T$. For $F = 0$, there are two saddle points in this region given by $t'_{\mathrm{SP}} \approx t \pm i(x-x')/\sqrt{-2E_e(R(t),0)}$. As x grows, they move away from t, and the adiabatic approximation eventually breaks down. The point x_{BO} where this happens can be estimated from $|t'_{\mathrm{SP}} - t| = T$. Substituting $E_e(R(t),0) \approx E_e(R_0,0) \equiv -\varkappa_e^2/2$ and noting that x' in Eq. (10) is restricted to the region of localization of $\psi_e(x'; R(t'))$, we obtain

$$x_{\mathrm{BO}} = \varkappa_e T = \frac{\varkappa_e}{2\omega_e} \propto M^{1/2}. \tag{12}$$

This is the distance by which an electron with velocity $\varkappa_e$ can depart from the nuclei before their positions change appreciably. In the region $|x| \ll x_{\mathrm{BO}}$, the electron has enough time to adiabatically adjust its state to the instantaneous position of the nuclei; that is, *retardation* caused by the finiteness of its velocity $\varkappa_e$ can be neglected. On the other hand, in the region $|x| \gtrsim x_{\mathrm{BO}}$, retardation becomes important and the adiabatic approximation breaks down. A similar situation in a time-dependent electric field was discussed in Ref. [27]. Thus, retardation is the reason for the breakdown of the BO approximation at large x. As seen from Fig. 2, Eq. (12) gives a good estimate of where this happens.

In the presence of a field, $F > 0$, the ground state turns into a Siegert state [9]. The solution of Eq. (1) is again sought in the form (7), where $f_v(x)$ vanish at $x \to \infty$ and satisfy the outgoing-wave boundary condition

$$f_v(x \to -\infty) = \frac{f_v m^{1/4}}{(2F|x|)^{1/4}}\exp\left[\frac{i}{3}(mF)^{1/2}(2|x|)^{3/2} + \frac{i[E(F)-\varepsilon_v](2m|x|)^{1/2}}{F^{1/2}}\right]. \tag{13}$$

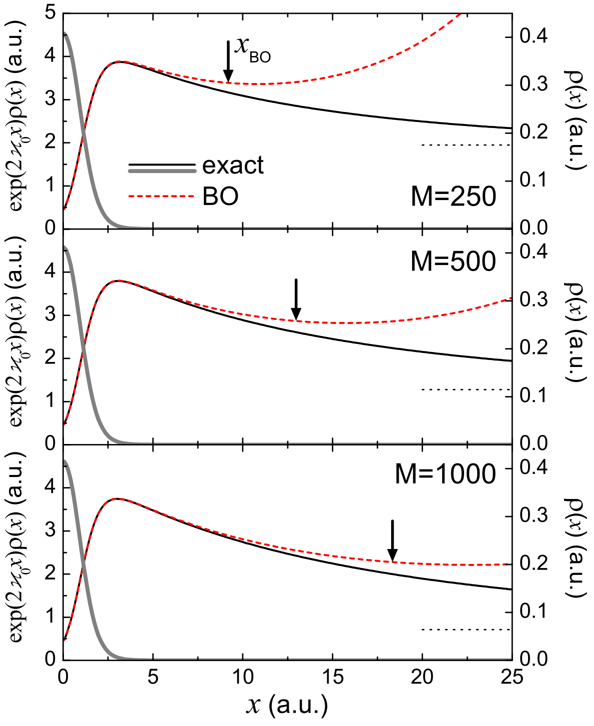

FIG. 2 (color online). Electron density [Eq. (9)] in the field-free ground state for three values of M. Solid (dashed) lines: exact results (BO approximation) for $e^{2\varkappa_0 x}\rho(x)$. Dotted lines: g_0^2, the value of $e^{2\varkappa_0 x}\rho(x)$ at $x \to \infty$. Arrows indicate the boundary of the region of validity of the BO approximation [Eq. (12)]. Thick gray lines: exact results for $\rho(x)$ (right-hand axis).

The equations for $f_v(x)$ in this case are solved by the SVD-based method developed in Ref. [28]. Similar boundary conditions can be written for Eq. (4). The energies $E(F)$, $E_e(R, F)$, and $E_{\rm BO}(F)$ are now complex. Their imaginary parts define the corresponding ionization rates, $\Gamma = -2{\rm Im}E$. We now consider realistic values of M equal to multiples of m_p. The results are shown in Fig. 3. To facilitate comparison of the exact and BO results, the ionization rate is divided by a rapidly varying field factor $W_0(F)$ defined in Eq. (15b). The BO approximation works very well at $F > F_{\rm BO}$, but rapidly departs from the exact results at $F < F_{\rm BO}$, and this is our second finding. To estimate the field $F_{\rm BO}$ where the BO approximation breaks down, we invoke the argument that has led us to Eq. (12). For $F > 0$, there are four saddle points contributing to the time integral in Eq. (10). For the BO approximation to hold in the tunneling problem, these points must satisfy $|t'_{\rm SP} - t| < T$ everywhere in the region $|x| < |x_F|$, where x_F is the turning point defined by $Fx_F = E_e(R(t), F)$. This requirement is most severe for $x = x_F$. In this case the saddle points coalesce pairwise at $t'_{\rm SP} \approx t \pm i\sqrt{-2E_e(R(t), F)}/F$ and move away from t as F decreases. Substituting $E_e(R(t), F) \approx -\varkappa_e^2/2$, the value of $F_{\rm BO}$ can thus be estimated by

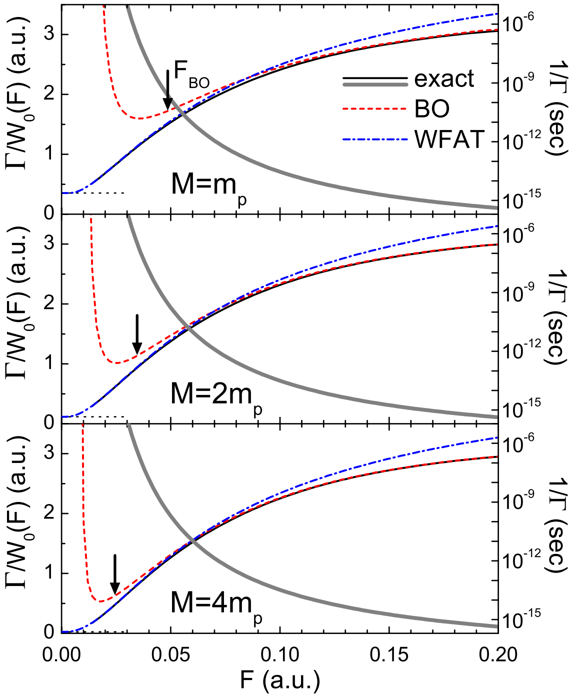

FIG. 3 (color online). Ionization rate of the ground state divided by $W_0(F)$ [Eq. (15b)] for three values of M. Solid (dashed) lines: exact results (BO approximation). Dashed-dotted lines: WFAT results [Eqs. (15)]. Dotted lines: g_0^2, the value of $\Gamma/W_0(F)$ at $F \to 0$. Arrows indicate the boundary of the region of validity of the BO approximation [Eq. (14)]. Thick gray lines: exact results for the lifetime $1/\Gamma$ (right-hand axis).

$$F_{\rm BO} = \frac{\varkappa_e}{T} = 2\omega_e\varkappa_e \propto M^{-1/2}. \qquad (14)$$

This is the field in which the time needed for an electron with initial velocity $\varkappa_e$ to reach the turning point x_F, taking into account its deacceleration by the field, is equal to T. At weaker fields, retardation breaks the validity of the BO approximation in the tunneling problem. As seen from Fig. 3, Eq. (14) works well. For H_2 ($M = m_p$) we have $F_{\rm BO} \approx 0.05$, which belongs to the range of intensities used in strong-field experiments [1]. The lifetime of the model H_2 at this intensity is $1/\Gamma \sim 10^{-10}$ sec. Thus the breakdown of the BO approximation for this molecule should be observable experimentally. In the general case, the effect is expected to be more pronounced for larger values of the adiabatic parameter $\epsilon \equiv \omega_e/I_p \propto F_{\rm BO}/F_c$, where $F_c \propto I_p^{3/2}$ is a boundary of over-the-barrier ionization. For example, $\epsilon_{N_2} \approx 0.6\epsilon_{H_2}$ and $\epsilon_{\rm CH} \approx \epsilon_{H_2}$, so the effect can be observable also in other molecules.

To investigate the behavior of the ionization rate at weak fields we employ the WFAT [9]. The coefficient f_v in Eq. (13) can be expressed in terms of the coefficient g_v in Eq. (8). By calculating the electronic flux, we obtain

$$\Gamma = \sum_v \Gamma_v, \quad \Gamma_v = |f_v|^2 = g_v^2 W_v(F)[1 + O(F)], \qquad (15a)$$

$$W_v(F) = \frac{\varkappa_v}{m}\exp\left(-\frac{2\varkappa_v^3}{3mF}\right). \qquad (15b)$$

Equation (15a) holds for $F \ll F_c$. The error term $O(F)$ indicates that this is an asymptotic expansion in F [7,8,10]. For frozen nuclei, this term for the dominant ionization channel corresponding to the smallest exponent in Eq. (15b) exceeds the exponentially suppressed contributions from electronically excited channels. In this case, only the dominant channel can be retained in Eq. (15a) [11]. In the problem with moving nuclei, however, another small parameter appears given by the electron-to-nuclear mass ratio $1/M$. The energy spacing of excited states becomes small, $\varepsilon_{v+1} - \varepsilon_v = O(M^{-1/2})$. The coefficients $g_v \propto \langle \phi_v | \chi \rangle$ are also affected: the maximum of the distribution g_v^2 shifts to larger $v = O(M^{1/2})$ as M grows (Fig. 4). All this changes the relative role of the different terms in Eq. (15a), and the contributions from higher channels now become more important than the term $O(F)$. In this case, all channels in Eq. (15a) should be retained. Such restructuring of the asymptotic expansion for the ionization rate of molecules is our third finding. Figure 3 shows that Eqs. (15) work very well up to $F \approx 0.1$. The term Γ_0 with the Oppenheimer exponent [for the present model $I_p = \epsilon_0 - E(0) = \varkappa_0^2/2m$] becomes dominant only at very weak fields.

To summarize, we have shown that retardation breaks the validity of the BO approximation in molecules at large electron-nuclei distances. As a result, the BO

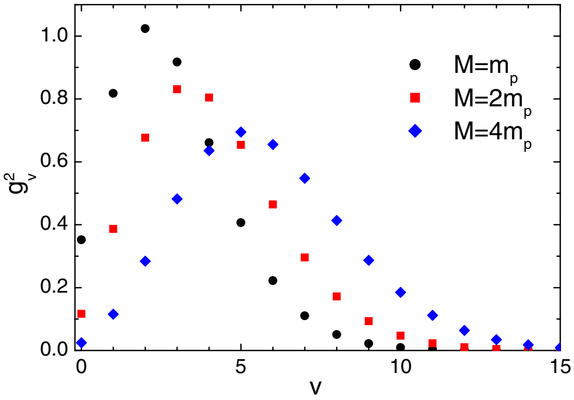

FIG. 4 (color online). Distribution of the coefficients g_v in Eqs. (8) and (15a) for the same M as in Fig. 3.

approximation does not correctly describe the electronic wave function in the field-free case at $x \gtrsim x_{\mathrm{BO}}$, even for the ground state. In the tunneling problem, it fails to predict the correct behavior of the ionization rate at weak fields $F \lesssim F_{\mathrm{BO}}$. Retardation reveals itself in the asymptotic tail of the electronic wave function, which probably has never been stressed before, but which is important in tunneling ionization and some other physical processes. In the typical situation $F_{\mathrm{BO}} \ll F_c$, so the properly restructured WFAT complements the BO approximation in the theory of tunneling ionization at weak fields.

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[1] F. Krausz and M. Ivanov, Rev. Mod. Phys. **81**, 163 (2009).
[2] J. R. Oppenheimer, Phys. Rev. **31**, 66 (1928).
[3] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics (Non-Relativistic Theory)* (Pergamon Press, London, 1958).
[4] B. M. Smirnov and M. I. Chibisov, Zh. Eksp. Teor. Fiz. **49**, 841 (1965) [Sov. Phys. JETP **22**, 585 (1966)].
[5] S. Yu. Slavyanov, Probl. Mat. Fiz. No. 4, 125 (1970) [English translation in *Topics in Mathematical Physics* (Consultants Bureau, New York, London, 1971), Vol. 4].
[6] T. Yamabe, A. Tachibana, and H. J. Silverstone, Phys. Rev. A **16**, 877 (1977).
[7] R. J. Damburg and V. V. Kolosov, J. Phys. B **11**, 1921 (1978).
[8] H. J. Silverstone, E. Harrell, and C. Grot, Phys. Rev. A **24**, 1925 (1981).
[9] O. I. Tolstikhin, T. Morishita, and L. B. Madsen, Phys. Rev. A **84**, 053423 (2011).
[10] V. H. Trinh, O. I. Tolstikhin, L. B. Madsen, and T. Morishita, Phys. Rev. A **87**, 043426 (2013).
[11] O. I. Tolstikhin, L. B. Madsen, and T. Morishita (unpublished).
[12] A. Saenz, Phys. Rev. A **66**, 063408 (2002).
[13] T. K. Kjeldsen and L. B. Madsen, Phys. Rev. A **71**, 023411 (2005).
[14] O. I. Tolstikhin, H. J. Wörner, and T. Morishita, Phys. Rev. A **87**, 041401(R) (2013).
[15] E. E. Nikitin and S. Ya. Umanskii, *Theory of Slow Atomic Collisions* (Springer-Verlag, Berlin, 1984).
[16] *Conical Intersections. Electronic Structure, Dynamics & Spectroscopy*, Advanced Series of Physical Chemistry Vol. 15, edited by W. Domcke, D. R. Yarkony, and H. Köppel (World Scientific, Singapore, 2004).
[17] G. Herzberg, Phys. Rev. Lett. **23**, 1081 (1969); U. Fano, Phys. Rev. A **2**, 353 (1970); M. J. Seaton, Rep. Prog. Phys. **46**, 167 (1983).
[18] Z. Mulyukov, M. Pont, and R. Shakeshaft, Phys. Rev. A **54**, 4299 (1996).
[19] M. Plummer and J. F. McCann, J. Phys. B **29**, 4625 (1996).
[20] X. Chu and Shih-I Chu, Phys. Rev. A **63**, 013414 (2000).
[21] L. Hamonou, T. Morishita, and O. I. Tolstikhin, Phys. Rev. A **86**, 013412 (2012).
[22] T. Tsogbayar and M. Horbatsch, J. Phys. B **46**, 085004 (2013).
[23] H. Wind, J. Chem. Phys. **42**, 2371 (1965).
[24] W. Kołos and L. Wolniewicz, J. Chem. Phys. **41**, 3663 (1964).
[25] O. I. Tolstikhin, S. Watanabe, and M. Matsuzawa, J. Phys. B **29**, L389 (1996).
[26] R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGraw-Hill, New York, 1965).
[27] O. I. Tolstikhin and T. Morishita, Phys. Rev. A **86**, 043417 (2012).
[28] P. A. Batishchev, O. I. Tolstikhin, and T. Morishita, Phys. Rev. A **82**, 023416 (2010).