Nonadiabatic polarization potentials in electron- and positron-molecule scattering: Application to $e^- + H_2$

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The nonpenetrating approximation appears to be the simplest way to allow one to incorporate nonadiabatic effects in the polarization potential calculated by means of the polarized orbital method. Unfortunately, this approximation is not well suited for an efficient implementation in quantum chemistry codes which, nowadays, use exclusively Gaussian-type orbitals. This computational limitation is remedied by replacing the incident point charge by a spherical Gaussian charge distribution, the exponent of which is suitably chosen. In so doing, we obtain a very efficient numerical algorithm that may be used with any molecular target regardless of its complexity or geometry. [S1050-2947(99)10201-4]

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I. INTRODUCTION

When studying low-energy electron- (positron-) molecule scattering, one of the main concerns is to elaborate computationally attractive methods which could be implemented and applied easily regardless of the size and complexity of the target. In the past few decades, several computational techniques have emerged as possible candidates, allowing one to investigate quantitatively various facets of electron (positron) scattering, especially those which are difficult to reach experimentally. In the context of time-independent formulation, there have been at least four important reviews and/or conference proceedings concerned with the theory and computational aspects of this subject [1–4]. These have reviewed a number of different methods, all with varying degrees of success and sophistication. The methods used are traditionally classified under one of two general headings: (1) numerical and (2) square integrable also known as L^2 methods. Although the boundaries between these approaches are quite blurred, the first category customarily encompasses linear-algebraic [5], single-center expansion [3,6,7], and partial differential approaches [8]. The second group of methods, i.e., L^2, mainly includes the R-matrix [9–15], complex Kohn [16], T-matrix [17,18], and so-called Schwinger-variational [19–22] procedures.

From a practical viewpoint, i.e., collisions of electrons with complex molecular targets larger than diatomics, the *ab initio* oriented Schwinger variational (SV) and R-matrix methods proved to be viable approaches which attracted much attention in the past few years. Without going into a detailed discussion of these methods, let us just recall that the former, which is inherently nonlocal, was designed to be accurate at the static-exchange level. As a consequence, in-corporating a local polarization potential into the SV numerical procedure becomes a hard task. The R-matrix method, also referred to as the dichotomic method, starts by partitioning the configuration space into several (at least two) regions. The $(N+1)$-particle problem is first solved within a finite box (e.g., bound-state calculation within a sphere of finite radius) but the scattering information is extracted by numerically propagating the scattering wave function from the surface of the box into the asymptotic region. The work on this procedure gave rise to the so-called U.K. scattering package [11]. Although this package is presently restricted to linear targets since it is based on ALCHEMY II [23], its extension to handle targets with arbitrary geometries is obviously feasible, especially by using Gaussian-type orbitals to represent the continuum functions describing the scattered electrons (positrons) [14]. As a consequence, we can conjecture that implementation of the ideas of the R-matrix method into a system such as GAUSSIAN or ACES II would normally lead in the near future to a package exhibiting the same high standard of efficiency already achieved in bound-state calculations. However, even though fully *ab initio* methods like SV or the R-matrix procedure are already available for use, they are computationally limited by the size of the targets since these calculations require very large basis sets in order to predict correct estimations of cross sections. As a useful alternative to the above *ab initio* oriented procedures, two less rigorous methods using a static-exchange-polarization potential received special attention, namely, the polarized orbital (PO) method originated by Temkin [24] and that of Gianturco and co-workers [4,25]. These two approaches, which rely upon *ad hoc* assumptions in order to simplify the mathematics, were successful for small diatomics [26,27] and simple polyatomics (generally symmetrical) [25,28,29].

The PO method [24,26,27,30–33] is probably the most straightforward method since it basically replaces the $(N+1)$-particle problem with a much more tractable problem of a single particle moving in a potential field. Unfortunately, this approach, which intrinsically is adiabatic, suffers drastically when the incident particle is in the close neighborhood of the target. As a matter of fact, in such a region the polarization potential calculated within the PO ansatz is known to be abnormally too strong, hence leading to incor-

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rect cross sections [34]. This major drawback was empirically corrected by Temkin and Lamkin [30], who proposed to ''turn off'' the coulombic interaction between the projectile and bound electrons whenever the former is within the target charge cloud. Although this procedure may seem a little crude, it is nonetheless founded on a physical idea (semiclassical) in which the projectile is supposed to acquire a comparable velocity to that of bound electrons once ''inside'' the target cloud. Consequently, within this region the incident particle is considered as if it had no noticeable effect on the polarization [33]. Temkin's method, which was successfully applied to modelize various electron-atom scattering processes, was also known as the nonpenetrating approximation. In the case of molecular targets, a variation of Temkin's prescription, called the better than adiabatic dipole (BTAD) method was thoroughly investigated and applied by Gibson and Morrison [27] to study $e^- + H_2$ and by Morrison, Saha, and Gibson for $e^- + N_2$ [35]. In this approach, the polarization potential is calculated using an interaction potential of the form $(r/s^2)P_1[(\mathbf{r}/r)\cdot(\mathbf{s}/s)]\delta(r<s)$, in which $\delta(r<s)$ is a step function. Unfortunately, the integrals needed to elaborate a computational procedure using the cutoff approximation, either BTAD or Temkin's, constitute a serious practical limitation especially for nonsymmetrical targets. Indeed, in such cases the scattering potential has to be evaluated on a relatively tight three-dimensional grid leading to very time-consuming calculations. More precisely, all the advantages provided by Gaussian-type orbitals (GTO's) are destroyed by the cutoff since the above-mentioned integrals are to be calculated within a finite sphere. As a consequence, it is no longer possible to use those integral transformations [36], allowing one to obtain efficient algorithms.

The present work aims at investigating an approach that is computationally attractive and suited for use on any molecular targets within the PO method. For such a purpose, we propose to replace the incident point charge by a smooth exponentially decaying charge distribution, i.e., of Slater or Gaussian type. However for obvious practical reasons, the natural choice is ultimately a spherical Gaussian charge density that is steadily made more diffuse as the projectile approaches the target. This approach allows one to avoid an integration over a finite sphere (which spoils the practical aspects of GTO's) since the interactions between the impinging particle and the target are weakened by adjusting the exponent which controls the spread of the distribution. As a first test of this method, we have investigated the reaction $e^- + H_2$, following closely the work of Gibson and Morrison [27]. Our calculated elastic cross sections are compared to the BTAD results of these authors as well as other investigators.

II. THEORY: AN OUTLINE

In the time-dependent approach to electron-molecule scattering, the objective is to solve the Schrödinger equation involving the following Hamiltonian:

$$\hat{\mathcal{H}}_T(\mathbf{r}_\alpha, \mathbf{R}_i, \mathbf{s}) = \hat{\mathcal{H}}_m(\mathbf{r}_\alpha, \mathbf{R}_i) + \mathcal{V}_{s-m} - \tfrac{1}{2}\nabla_s^2, \qquad (1)$$

in which $\hat{\mathcal{H}}(\mathbf{r}_\alpha, \mathbf{R}_i)$ represents the Hamiltonian of the isolated molecule depending only on the coordinates of the bound electrons $\{\mathbf{r}_\alpha\}_{\alpha=1,2,\ldots,N_e}$, and those of the nuclei $\{\mathbf{R}_i\}_{i=1,2,\ldots,N_n}$. The interaction of the projectile with the electrons and the nuclei of the target molecule is accounted for by $\mathcal{V}_{s-m}$, which is explicitly defined by

$$\mathcal{V}_{s-m} = \underbrace{\sum_{\alpha=1}^{N_e}\frac{1}{|\mathbf{r}_\alpha - \mathbf{s}|}}_{\mathcal{V}_{s-e}} - \underbrace{\sum_{i=1}^{N_n}\frac{Z_i}{|\mathbf{R}_i - \mathbf{s}|}}_{\mathcal{V}_{s-N}} \qquad (2)$$

In order to simplify the mathematics, it is customary (though not always justified) [2] to introduce various approximations the most important of which is the so-called fixed nuclei approximation (FNA). As a consequence, one will have to solve the equation

$$[\hat{\mathcal{H}}\mathcal{H}^{(e)}(\mathbf{r}_\alpha,\mathbf{s};\mathbf{R}_i) - E]\Psi(\mathbf{r}_\alpha,\mathbf{s};\mathbf{R}_i) = 0, \qquad (3)$$

in which the Hamiltonian $\hat{\mathcal{H}}^{(e)}$ describes the motion of the electrons in the field of fixed nuclei and is written as

$$\hat{\mathcal{H}}^{(e)}(\mathbf{r}_\alpha, \mathbf{s};\mathbf{R}_i) = \hat{\mathcal{H}}_m^{(e)}(\mathbf{r}_\alpha, \mathbf{R}_i) + \mathcal{V}_{s-m} - \tfrac{1}{2}\nabla_s^2, \qquad (4)$$

where the coordinates of the nuclei, $\{\mathbf{R}_i\}$, now appear as parameters whose values are fixed in advance. In what follows, these parameters will deliberately be omitted from the definition of the wave functions in order to avoid unnecessary complicated expressions.

Now that we have written the formal Schrödinger equation describing the problem under study, it is time to make the very difficult decision as regards the computational procedure that should be used for solving Eq. (3). In the present investigation, we will be using the PO method, which, according to the introductory remarks, proved to be very useful for the modelization of $e^- +$ atom, $e^- + H_2$, and $e^- + N_2$ collisions. As a starting point of the PO method, the $(N_e + 1)$-particle wave function is assumed to have the form

$$\Psi(\mathbf{r}_\alpha, \mathbf{s}) = \tilde{\mathcal{A}}[\Psi^{(d)}(\mathbf{r}_\alpha; \mathbf{s})\Phi(\mathbf{s})], \qquad (5)$$

in which, $\Psi^{(d)}(\mathbf{r};\mathbf{s})$ represents the N_e-particle wave function of the target as distorted by a stationary external charge located at $\mathbf{s}$, while $\Phi(\mathbf{s})$ describes the scattered particle. The operator $\hat{\mathcal{A}}$ antisymmetrizes the function $\Psi(\mathbf{r}_\alpha, \mathbf{s})$ with respect to the interchange of any bound electrons with the scattered one. Before going into further details, it should be noted that if exchange were not allowed, the above definition would be formally analogous to the wave function obtained in the framework of the FNA in the sense that both of them are intrinsically adiabatic. To be more specific, Eq. (5) expresses the idea that the motion of the bound electrons and that of the projectile remain constantly uncoupled no matter how closely the projectile approaches the molecule. This nonadiabaticity may also be depicted by saying that the electron density of the molecule is allowed to adjust its shape instantaneously (i.e., bound electrons moving at high velocity) in such a way as to minimize the repulsions with the impinging particle (i.e., low energy). Obviously, even in low-energy scattering, this model is only valid when the projectile is far enough from the target, and is expected to break down as soon as the incident particle closely approaches the

molecule. The experimental evidence of such a situation is the possible existence of a ''stable'' anionic species during the collision process, in which case all the electrons are to be treated on an equal footing. In their attempt to remedy this problem, Temkin and Lamkin [30] suggested taking nonadiabatic effects into account by empirically modifying the form of the interaction potential $\mathcal{V}_{s-e}$ of Eq. (2). More explicitly, $\mathcal{V}_{s-e}$ is multiplied by a step function which ''shuts down'' the interaction, i.e., $\mathcal{V}_{s-e}=0$, inside the sphere centered on the center of mass (COM), and limited by the location of the projectile. This yields

$$\mathcal{V}_{s-m}^{T} = \sum_{\alpha=1}^{N_e} \frac{\delta(r_\alpha < r)}{|\mathbf{r}_\alpha - \mathbf{s}|} - \sum_{i=1}^{N_n} \frac{Z_i}{|\mathbf{R}_i - \mathbf{s}|}, \quad (6)$$

where $\delta(r_\alpha < r)$ is a Boolean-type function (step function) such that it is equal to 1 if its argument were true, and 0 otherwise. It should be pointed out that even when $\mathcal{V}_{s-m}$ is weakened by means of the above procedure, the corresponding polarization potential still exhibits a strong attraction at small and intermediate radial distances [27]. This behavior is, once more, corrected empirically by dropping selected terms from the expansion of $\mathcal{V}_{s-e}^{T}$ in terms of Legendre polynomials. There is a compelling theoretical reason for dropping the monopole [27], at least when the projectile is outside the target cloud, in which case the monopole cancels out in the polarized and unpolarized energies. However, for the other terms (except the dipole) the reasons are rather obscure, since they do not have any theoretical justifications. The dipole term, which is the only term appearing in the BTAD approximation, is always kept since it ensures a correct long range decrease, i.e., $1/r^4$, of the polarization potential:

$$\mathcal{V}_{s-m}^{BTAD} = \frac{r}{s^2} P_1\left[\frac{\mathbf{r}\cdot\mathbf{s}}{rs}\right] \delta(r<s) - \sum_{i=1}^{N_n} \frac{Z_i}{|\mathbf{R}_i - \mathbf{s}|}. \quad (7)$$

Thus far, we have made some general comments regarding the PO method and the polarization potential obtained from the adiabatic form of the wave function introduced in Eq. (5). In the following, we will briefly review how the polarization potential enters the scattering equation, and give its explicit definition as obtained in the framework of the PO method. Basically, the derivation of the scattering equation is carried out by requesting that the projection of Eq. (3) over the unperturbed wave function satisfies

$$\langle \Psi^{(0)}(\mathbf{r}_\alpha) | \hat{\mathcal{H}}^{(e)}(\mathbf{r}_\alpha, \mathbf{s}) - E | \Psi(\mathbf{r}_\alpha, \mathbf{s}) \rangle = 0, \quad (8)$$

where $\Psi^{(0)}(\mathbf{r}_\alpha)$ is the unperturbed function describing the isolated target. According to Drachman and Temkin [26], this is a necessary condition for $\Psi(\mathbf{r}_\alpha, \mathbf{s})$ to satisfy the Schrödinger equation, but is not sufficient. However, these authors also reported that use of the above equation yields rather satisfactory results provided that the perturbed target function $\Psi^{(d)}(\mathbf{r}_\alpha; \mathbf{s})$ is good enough. Thus, starting with Eq. (8), one obtains, after some algebra, an ''adiabatic'' scattering equation which reads

$$[-\tfrac{1}{2}\nabla_s^2 + V_s + V_p^{AD} - \tfrac{1}{2}k^2]\Phi(\mathbf{s}) = \text{exchange terms}, \quad (9)$$

where the static and the polarization potentials, respectively, are defined as follows:

$$V_s(\mathbf{s}) = \langle \Psi^{(0)}(\mathbf{r}_\alpha) | \mathcal{V}_{s-m} | \Psi^{(0)}(\mathbf{r}_\alpha) \rangle, \quad (10)$$

$$V_p^{AD}(\mathbf{s}) = \underbrace{\left\langle \Psi^{(d)}(\mathbf{r}_\alpha; \mathbf{s}) \left| \widehat{\mathcal{H}}^{(e)}(\mathbf{r}_\alpha) + \mathcal{V}_{s-m} \right| \Psi^{(d)}(\mathbf{r}_\alpha; \mathbf{s}) \right\rangle}_{E^{(d)}} - E^{(0)} - V_s \quad (11)$$

where $E^{(0)}$ and $E^{(d)}$, respectively, are the energies of the isolated target and when subjected to the field of a point charge located at $\mathbf{s}$. In the case of many electron targets, these energies are variationally determined using the well-known Hartree-Fock-Roothaan procedure. The first of the above equations, i.e., the static potential, is in fact the first-order perturbation of the energy due to the potential $\mathcal{V}_{s-m}$. Accordingly, the full adiabatic polarization given by Eq. (11) includes all the corrections of the energy starting with $E^{(2)}$ and going up to $E^{(\infty)}$.

To close this section, it should be mentioned that when calculated from Eq. (11), the strength of V_p^{AD} is overestimated as soon as the projectile closely approaches the target. The nonpenetrating procedure attempts to correct this defect by empirically incorporating some of the nonadiabatic effects in the definition of the polarization potential. For such a purpose, the full Coulomb potential $\mathcal{V}_{s-m}$, occurring in Eq. (11) is replaced by that of Temkin [Eq. (6)] or by that of the BTAD method [Eq. (7)].

III. COMPUTATIONAL PROCEDURE

In the framework of the BTAD or more generally the nonpenetrating PO method, the determination of the cross sections is generally carried out in two major steps. The first of these consists in determining the scattering potential V^{SCAT} acting on the projectile, while the second addresses the resolution of the corresponding equation (9).

Among the most cumbersome tasks in evaluating V^{SCAT} is the elaboration of a reliable numerical procedure allowing one to generate the following matrix elements:

$$\mathcal{I}^{\mathrm{NP}} = \langle g_{i,j,k}[\zeta_1, |\mathbf{r}-\mathbf{a}|^2]|\mathcal{V}_{s-e}^{\mathrm{BTAD}}|g_{i',j',k'}[\zeta_2, |\mathbf{r}-\mathbf{a}|^2]\rangle_{0 \le r \le s}$$
$$(12)$$

where the integration is carried out inside a sphere centered on the COM, and such that $r \le s$. The location of the GTO's may be the same, i.e., $\mathbf{a} = \mathbf{b}$, in which case the above integral reduces to a two-center one-electron integral. For numerical purposes, the above integrals may be evaluated either analytically by means of some series expansion, or numerically using a hybrid method involving both analytical and numerical integration [27]. To be more specific, Gibson and Morrison first expanded the GTO's $g_{i,j,k}$ and $g_{i',j',k'}$ in terms of spherical harmonics, making the integration over θ and ϕ very straightforward. The remaining integral, i.e., over r, is finally carried out using a numerical scheme, namely, a fixed step-size trapezoidal quadrature. However, in either of these computational strategies the time expense is expected to increase dramatically when dealing with large molecular targets even when more sophisticated integration techniques are applied to carry out the radial integrals.

As pointed out in Sec. I, it should be remembered that all of the practical advantages of GTO's, in simplifying the calculations of molecular integrals and hence making GTO-based quantum chemistry codes so efficient, are to a large extent destroyed by Temkin's cutoff. Indeed, because the radial integration is carried out within a finite sphere, it is no longer possible to use those integral transformations [36] which allow one to obtain rapid and reliable algorithms for the evaluation of multicenter integrals. Consequently, when large nonsymmetrical molecular systems are considered (for which the potentials, i.e., static, polarization, and exchange, are calculated over a very large number of grid points), use of the cutoff procedure exhibits serious practical limitations. An interesting alternative to Temkin's prescription is to replace the impinging point charge by a normalized spherical Gaussian charge distribution giving rise to the interaction potential:

$$V_{s-m}^{\mathrm{GTO}}(\mathbf{s}; \zeta_s) = \sum_{\alpha=1}^{N_e} \left\langle \frac{\rho(\zeta_s, |\mathbf{r_s}-\mathbf{s}|^2)}{|\mathbf{r}_\alpha - \mathbf{r}_s|} \right\rangle_{\mathbf{r}_s}$$
$$- \sum_{i=1}^{N_n} Z_i \left\langle \frac{\rho(\zeta_s, |\mathbf{r_s}-\mathbf{s}|^2)}{|\mathbf{R}_i - \mathbf{r}_s|} \right\rangle_{\mathbf{r}_s}, \quad (13)$$

in which $\langle \cdots \rangle_{\mathbf{r}_s}$ indicates that the integration is performed over the variable $\mathbf{r}_s$ and where $\rho(\zeta_s, |\mathbf{r}_s-\mathbf{s}|^2)$ is a spherical Gaussian charge distribution such that

$$\rho(\zeta_s, |\mathbf{r}_s-\mathbf{s}|^2) = (2\zeta_s/\pi)^{3/2} \exp(-2\zeta_s|\mathbf{r}_s-\mathbf{s}|^2), \quad (14)$$

where ζ_s is an adjustable parameter. It is clear that the above definition may be made more flexible and hence improve our results by expressing the density $\rho(\zeta_s, |\mathbf{r}_s-\mathbf{s}|^2)$ as a linear combination of spherical Gaussians with more variational parameters. However, at this stage of our work this generalization would be too ambitious, since one first needs to elaborate the automatic procedure allowing the exponents to be adequately chosen.

The analytical form of the new interaction (13) deserves few comments. First, the above defined potential is smooth everywhere, which makes it more consistent with the continuity principle of quantum mechanics [31] as compared to the cutoff. It should, however, be pointed out that according to Drachman and Temkin [26], the noncontinuous step function of Eqs. (6) and (7) may be regarded as the leading term of the series representation describing a smooth cutoff. Second, if the exponent ζ_s is large enough, the potential V_{s-m}^{GTO} will ultimately mimic the interaction potential of a point charge with the target. In other words, this would lead to the well-known adiabatic potentials. Finally, in contrast to Temkin's procedure, the above potential does not necessarily enforce the polarization to vanish in the COM (unless one chooses the value $\zeta_s = 0$, in which case there is no projectile). As a matter of fact, in the case of molecules there is no physical evidence for a zero polarization in the COM. More precisely, in the neighborhood of the COM, where short-range effects are normally dominant, it suffices to adjust the exponent so as to obtain a sufficiently weak polarization.

Regarding the exchange term, i.e., the right-hand side of Eq. (9), it will be approximated by the so-called Hara free-electron-gas model potential (HFEG). This procedure was thoroughly discussed by Morrison and Collins [37]. The advantage of this strategy is the ease of its computational implementation, which is made possible by the removal of the nonlocality that is intrinsically built into the exact exchange potential. More specifically, the HFEG model exchange is defined by

$$V_{ex}^{\mathrm{HFEG}} = -(2/\pi)k_F(\mathbf{s})\mathcal{F}[\eta(\mathbf{s})], \quad (15)$$

in which $k_F(\mathbf{s})$ is the Fermi momentum, and where the function $\mathcal{F}$ is defined as

$$\mathcal{F}[\eta(\mathbf{s})] = \frac{1}{2} + \frac{1-\eta^2(\mathbf{s})}{4\eta(\mathbf{s})} \ln\left|\frac{1+\eta(\mathbf{s})}{1-\eta(\mathbf{s})}\right|, \quad (16)$$

with

$$\eta(\mathbf{s}) = \frac{k(\mathbf{s})}{k_F(\mathbf{s})} \quad \text{and} \quad k_F(\mathbf{s}) = [3\pi^2\rho(\mathbf{s})]^{1/3}, \quad (17)$$

where the local momentum $k(\mathbf{s})$ is related to the ionization energy according to the relation $k^2(\mathbf{s}) = 2(E_{\mathrm{inc}}+I) + k_F^2(\mathbf{s})$, in which $E_{\mathrm{inc}} = k^2/2$ is the energy of the incident particle while I is the ionization potential of the target molecule. Although I is defined as the ionization potential, it is in fact used as an adjustable parameter for tuning the HFEG [37]. Consequently, the numerical value attached to I is in fact case dependent. In the present work we use the tuned value of Gibson and Morrison [27], namely, $I = 2.27$ eV.

The second step of the present electron-molecule scattering computational procedure is to extract the cross sections by solving Eq. (9). For such a purpose it is customary, at least for small molecules, to expand the scattering wave function $\Phi(s)$ in terms of spherical harmonics. This yields the following coupled differential equations for the radial part:

$$\left[\frac{d^2}{ds^2} - \frac{l(l+1)}{s^2} + k^2\right]f_l^m(s)$$

$$= 2\sum_{l'=0} \langle Y_l^m(\theta,\varphi)|V^{\text{SCAT}}(\mathbf{s})|Y_{l'}^m(\theta,\varphi)\rangle f_{l'}^m(s),$$

$$(18)$$

where $Y_l^m(\theta,\varphi)$ represent surface spherical harmonics and the scattering potential $V^{\text{SCAT}} = V_s + V_p + V_{\text{ex}}$. For numerical purposes, the coefficients of the right-hand side are evaluated by expanding the scattering potential in terms of spherical harmonics which in the case of linear molecules (lying on the $\mathbf{Z}$ axis) reduce to Legendre polynomials. As a consequence, the RHS of the above equation may be written as

$$\sum_{l'=0} \left[\sum_{\lambda=|l-l'|}^{l+l'} \sqrt{\frac{2\lambda+1}{4\pi}}\langle lm|\lambda 0|l'm\rangle V_\lambda^{\text{SCAT}}(s)\right]f_{l'}^m(s),$$

$$(19)$$

where $\langle l_1 m_1|l_2 m_2|l_3 m_3\rangle$ denotes the so-called Gaunt coefficients (also related to Clebsch-Gordon's. See Ref. [38], p. 751). The symbol Σ'' indicates that the summation is to be carried out with a step of 2. The coefficients $V_\lambda^{\text{SCAT}}(s)$ are determined by a numerical integration according to

$$V_\lambda^{\text{SCAT}}(s) = \frac{2\lambda+1}{2}\int_{-1}^{1} V^{\text{SCAT}}(\mathbf{s})P_\lambda(x)dx$$

$$= \sum_{i=1}^{n} w_i V^{\text{SCAT}}(\mathbf{s}_i)P_\lambda(x_i), \qquad (20)$$

where $\{w_i\}_{1\le i\le n}$ and $\{x_i\}_{1\le i\le n}$ are the weights and the roots of the Gauss-Legendre quadrature, *a priori* chosen to be used for the calculation of the coefficients $V_\lambda^{\text{SCAT}}(s)$. Accordingly, the set of vectors $\{\mathbf{s}_i\}_{1\le i\le n}$ corresponds to the location of the projectile such that $s_i = (s,\theta_i)$. In practice, the values of the scattering potential are first calculated over a polar grid in which each ray corresponds to a root of the Gauss-Legendre quadrature used in Eq. (20).

IV. RESULTS AND DISCUSSION

In this section, we will essentially compare the numerics obtained with the procedure presented above and those of the BTAD approximation. The molecular system we are considering is H_2, which, somehow, constitutes a necessary stop before going into any other investigation. As a first instance (Fig. 1) we have calculated the full Gaussian polarization potential for an exponent ζ_s varying linearly with the distance s separating the projectile from the COM, i.e., $\zeta_s = \beta s + \epsilon$, and such that $\epsilon\to 0$. In so doing we enforce the polarization to be very small in the neighborhood of the COM, and in the meantime increase the contraction of the Gaussian density once far enough so as to mimic a point charge. As may be seen, the polarization potential becomes stronger in the region of interest (i.e., short and intermediate separations) for increasing values of β. The upper limit, of course, is the full adiabatic polarization for which $\beta\to+\infty$. From a physical viewpoint, this amounts to saying that the
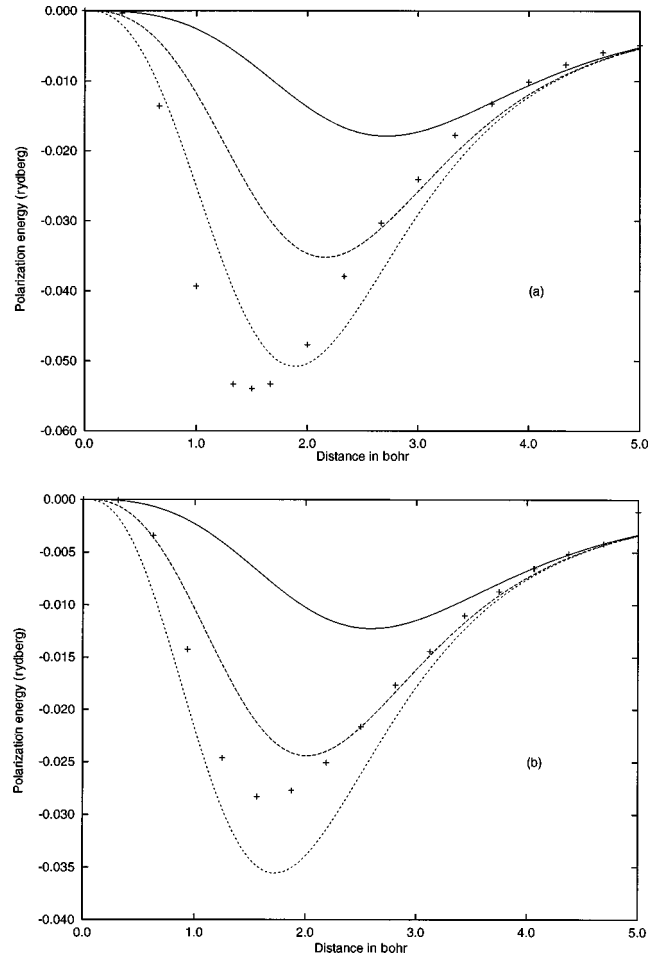

FIG. 1. Comparison of the BTAD and the full Gaussian polarizations along the $\mathbf{Z}$ (a) and $\mathbf{X}$ (b) axes. Continuous curves correspond to $\beta=0.1$ (solid line), $\beta=0.2$ (long dashes), and $\beta=0.3$ (points). Values indicated by pluses are from Ref. [27].

projectile which at infinity behaves as a point charge (described by a highly contracted Gaussian density) steadily becomes more ''delocalized'' (corresponding to a more diffused Gaussian charge density) while approaching the target. Obviously, when close to the COM, our proposed choice for ζ_s yields a very diffused charge density because we are trying to compensate for the strong distortion of the target (re-

TABLE I. Integrated cross sections for selected values of the incident energy. In Eq. (13), the exponent is assumed to have the form $\zeta_s = \beta s + \eta$ in which s is the separation of the projectile from the center of mass while $\eta\approx 0$. Following Gibson and Morrison (Ref. [27]), the moments defined by of Eq. (20) are evaluated using a Gauss-Legendre quadrature of order 7.

E (in Ry)	$\beta=0.1$	$\beta=0.2$	$\beta=0.3$	$\beta=0.4$	$\beta=0.5$	Table IV of Ref. [27]
0.1	41.929	39.942	38.168	36.742	35.275	32.939
0.09	54.910	55.788	56.180	56.340	56.421	52.356
0.20	55.343	59.200	61.868	63.890	65.527	60.330
0.36	47.552	51.642	54.419	56.454	58.026	54.172
0.64	33.957	36.771	38.716	40.145	41.248	39.073
1.00	23.238	25.090	26.430	27.445	28.247	26.960

sulting from that of the adiabatic approximation) by an increase in the spread of the incident charge density. Here it is of interest to note that the present procedure is, from a distance, similar to the time-dependent description of electrons scattering in which the incident particle polarizes the target which in turn acts back on the projectile by modifying the wave packet accompanying it.

Practically, using the same atomic basis as Gibson and Morrison (cf. Table I of Ref. [27]), in Fig. 1 we plot the full Gaussian polarization for some selected values of β. It can be seen that, along the **Z** axis, the value $\beta=0.30$ yields a quite similar polarization to that obtained in the BTAD approximation; however, in the **X** direction, BTAD results are bracketed by the potentials corresponding to $\beta=0.2$ and 0.3. This comparison indicates that ζ_s should not only depend on the separation between the projectile and the COM but also on the angle $\theta_s=(\widehat{\mathbf{Z},\mathbf{s}})$. Furthermore, we can conjecture at this stage that the value $\beta=0.30$ would normally lead to reasonable elastic cross sections for the case under study, since in both directions our Gaussian polarization is comparable to the BTAD.

In Table I we list some values of integrated cross sections for some selected values of the incident energy which were obtained using the parameters gathered in Table II. These values seem to indicate that, for low incident energies, the cross sections increase when β decreases. This situation is reversed for large values of E_{inc}, where larger β's yield larger total cross sections. The discrepancy between our values and those of Ref. [27] appears to be a problematic situation for small incident energies.

In order to have a fairly good idea of the behavior of the present method, in Fig. 2 we plot our calculated values of total elastic cross sections using the symmetries $\Sigma_{g,u}$, Π_u, and $\Delta_{g,u}$, as well as those given previously by other investigators. From this figure, it is clear that our choice of $\beta=0.30$ is rather satisfactory in the region (3 eV, 10 eV), since our cross sections are in good agreement with the results of the BTAD approximation and more importantly with experimental results of Jones [39]. However, in spite of the discrepancies for small values of E_{inc}, this comparison is quite encouraging, since we should remember that our choice of the form of the exponent ζ_s was done in a somewhat heuristic manner. In other words, one may expect that a more careful choice of this parameter would allow us to improve our results. Note has to be taken that, from a computational point of view, this method remains far more efficient than one using the nonpenetrating procedure.

V. CONCLUDING REMARKS

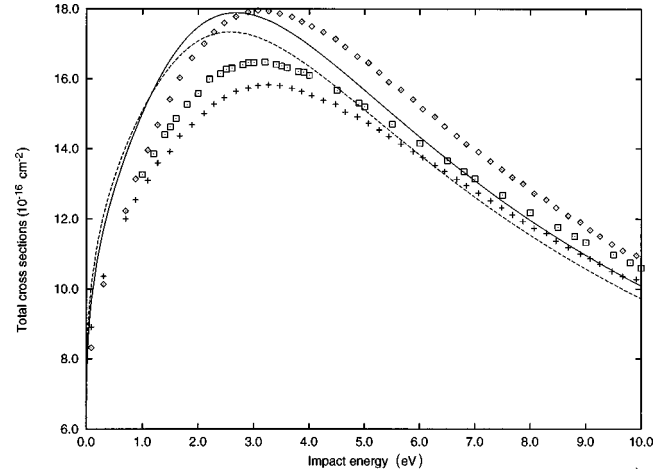In this work, we have investigated an alternative method allowing one to obtain a well-behaved polarization for short

FIG. 2. Comparison of calculated cross sections using the symmetries $\Sigma_{g,u}+\Pi_u+\Delta_{g,u}$ with those of previous theoretical and experimental investigations. Smooth curves were obtained with $\beta=0.3$ (solid line) and $\beta=0.2$ (long dashes). Pluses are from Gibson and Morrison (Ref. [27]), diamonds from Henry and Lane (Ref. [40]), and squares are the experimental values of Jones (Ref. [39]) (for $E_{\text{inc}}\geqslant1$ eV).

and intermediate separations, that has the great advantage of being efficiently implementable in *ab initio* quantum chemistry codes. Indeed, replacing the incoming particle by a spherical Gaussian charge distribution (with a suitably chosen exponent ζ_s) enables us to describe the interaction projectile and/or molecule by means of well-known integrals (efficiently computed since they involve GTO's over the whole space). Obviously, for a large value of ζ_s, our approach reproduces the results of the full adiabatic approximation. For short and intermediate separations the interaction projectile and/or target is weakened by making the charge distribution more and more diffused (choosing a small value for ζ_s). This strategy yields a polarization potential which, to a good extent, is similar to that obtained using the BTAD [27] approximation. However, like any parametrized method, the present approach requires tuning the exponent ζ_s so as to obtain an acceptable scattering potential. This point still needs further investigations to establish a systematic procedure allowing us to make the best guess for such a parameter. Although such an issue will hopefully be settled as we gain more experience with our method, we can conjecture that such a procedure will probably use the overlap between the charge distribution and the target as a criterion leading to a ''good'' value of ζ_s. Nevertheless, the initial results reported in this work seem to be encouraging enough so as to motivate further applications of this approach in order to develop a computational intuition from which we can, if no other choice is given, elaborate an em-

TABLE II. Summary of the parameters used in the present investigation.

In Eq. (20)	$\lambda_{\text{max}}=6$ and $n=7$ [a]
In Eq. (15)	$I=2.27$ eV [a]
$\alpha_{\parallel}=-2V_p^{G_{\text{TO}}}(0,0,z)z^4$	6.637 42 at $z=10$ a.u.
$\alpha_{\perp}=-2V_p^{G_{\text{TO}}}(x,0,0)x^4$	4.515 14 at $x=10$ a.u.
Basis set for the calculation of V_s, $V_p^{G,\text{TO}}$, and V_{ex}	GM [a] (Table I)

[a]As used in Ref. [27].

pirical method for the determination of ζ_s. Finally, it is also important to test the present approach on large molecules in order to determine how sensitive the results are to the changes in the value of such a parameter.

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