Procedure for correcting variational *R*-matrix calculations for polarization response

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Using standard bound-state methodology, variational calculations of molecular *R* matrices can severely underestimate polarization response in the near-target region inside the *R*-matrix boundary. An "ΔR" procedure is proposed here as an easily implemented but significant improvement of such *R* matrices. The efficacy of this procedure is demonstrated in calculations of differential and integral cross sections for vibrationally elastic e-CO_2 scattering at and below 1 eV.

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I. INTRODUCTION

The *R*-matrix method is a well-established, robust procedure for calculating cross sections for electron scattering from atoms and molecules [1]. At the heart of the application of this method to molecular targets are fixed-nuclei (FN) variational calculations at a specified total energy E within the "*R*-matrix box"—typically a sphere of radius r_1 that encloses the N-electron target—using quantum-chemistry codes originally developed for bound-state structure problems [2,3]. The radius r_1 is usually chosen to be twice (or more) the effective target radius r_0. By interpolating the resulting FN *R* matrices in energy and internuclear separation R, one can construct the *vibronic R* matrix $\mathbb{R}(r_1)$ via the energy-modified adiabatic phase-matrix (EMAP) method [4,5] or, if nonadiabatic effects are important, the nonadiabatic phase-matrix method [6,7]. Outside the box, efficient analytic methods are used to solve the rovibronic coupled equations of the electron-molecule system, yielding the desired asymptotic scattering quantities [8].

While variational calculations for $N+1$ electrons inside the effective target radius r_0 are comparable to well-established bound-state calculations, the extension to the much larger box radius r_1 can be a formidable obstacle to converged calculations that correctly represent the polarization response. For a polyatomic target, bound-state variational methods using Gaussian basis functions can be adapted to variational *R*-matrix calculations [2]. By representing the partial-wave open-channel orbitals which extend to the *R*-matrix boundary r_1 by a fixed Gaussian expansion [3], one can include bound-free exchange effects accurately. Moreover, static multipole moments can be determined to sufficient accuracy within the effective radius r_0 to determine accurately the electron-static multipole potentials. But

closed-channel orbitals that couple to virtual excitations of the target cannot easily be represented in a Gaussian basis, because such orbitals decay as inverse powers of r, much less rapidly than the decay of Gaussian functions. So one might expect that Gaussian basis sets designed for bound-state calculations could not accurately represent the polarization response outside the effective target radius r_0. Unless polarization pseudostates and explicit closed-channel orbitals are included in a variational calculation, this problem affects any *R*-matrix calculation using a Gaussian orbital basis. This observation motivates our development of the ΔR procedure (DRP).

This method, which we describe in Sec. II, is a simple, systematic algorithm for correcting any *R* matrix that inadequately represents the polarization response in the near-target region $r_0 \le r \le r_1$. In Sec. III we illustrate this method with calculations of cross sections for e-CO_2 scattering at and below 1.0 eV. In this energy range, these cross sections are very sensitive to the polarization response of the target and to a virtual state.

II. THEORY

Assuming one has constructed a variational representation that adequately represents exchange and correlation within the effective target radius r_0, and bound-free exchange and static multipole potentials inside the *R*-matrix box r_1, the crucial problem is to correct bound-free correlation (polarization response) in the *near-target region* $r_0 \le r \le r_1$. The first step in the DRP is the construction of a set of effective *R* matrices at r_0 by propagating a given FN variational *R*-matrix *inward* from r_1, using as the potential energy one's best estimate of the effective potential in the near-target region from the original FN variational calculations.

The second step is *outward* propagation of each of these effective *R* matrices from r_0 to r_1. If in this outward propagation one used the *same* external potential as in the first step, one would merely regain the original FN variational *R*

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matrix at r_1. In the DRP, however, this external potential is replaced in the outward propagation step by a local potential, based either on theory or experiment, designed more accurately to represent the polarization response in the near-target region. (Since R-matrix propagation requires local potentials [8], it cannot incorporate bound-free exchange effects. But, in the DRP scheme, information regarding these effects that was in the original FN R matrices is retained through the inward-outward propagation.) In the present implementation, for example, we used the permanent quadrupole potential $-Q(R)/r^3 P_2(\cos\theta)$ for the inward propagation, and the asymptotic potential

$$V_{\mathrm{asy}}(r;R) = -\frac{\alpha_0(R)}{2r^4} - \left[\frac{\alpha_2(R)}{2r^4} + \frac{Q(R)}{r^3}\right] P_2(\cos\theta) \tag{2.1}$$

for the outward propagation. Here θ is the lab-frame scattering angle, and $Q(R)$, $\alpha_0(R)$, and $\alpha_2(R)$ are the permanent quadrupole moment and the induced spherical and nonspherical polarizabilities of the target.

In principal, the DRP replaces the effect of an inadequate near-target polarization potential in the original variational calculations by one more suited to polarization in this region. The result is a vibronic R matrix at r_1 that incorporates the physical effects of the polarization response of the target more accurately than one calculated directly from the original FN R matrices.

The outward-propagation step is an application of the asymptotic-distorted-wave (ADW) method [9,10] to the set of scattering channels included in the original variational R matrices. For electronically elastic scattering in a body-fixed reference frame in the FN approximation, these channels are identified by l, the orbital angular momentum of the scattering electron; and Λ, its projection on the internuclear axis. The ADW method was designed to augment FN variational R matrices with elements corresponding to angular momentum quantum numbers l and Λ of higher order than those in the original calculation. In an ADW R-matrix propagation, one uses multichannel potential functions with the correct long-range behavior, and includes off-diagonal potentials that couple open-channel target states to closed-channel pseudostates. Because such a propagation is formally equivalent to solving the FN close-coupling equations without exchange, the ADW method is justified only for partial waves whose inner classical turning point is greater than r_0 [9]. The present application of this method to the artificial R matrix at r_0, constructed via DRP inward propagation, for low-order partial waves, is justified, as argued above, because information on bound-free exchange is reinstated in the subsequent outward propagation. The ideal methodology would be to propagate each original R matrix inward to r_0, augment it there by a diagonal matrix of free-scattering partial wave elements as in the ADW method [9], and then propagate the resulting enlarged R matrix outward to r_1.

In the calculations reported here, we used standard procedures in the external region ($r > r_1$) to determine scattering quantities from the vibronic R matrix [8,11]. For calculations

of vibrationally inelastic differential cross sections (DCS's), convergence of sums over quantum numbers l and Λ is crucial. To ensure such convergence, we use Born completion [12–15] to analytically complete these sums (to infinity). Thus the elastic DCS can be written

$$\frac{d\sigma}{d\Omega} = \frac{d\sigma^B}{d\Omega} + \left(\frac{d\sigma^{\mathrm{VAR}}}{d\Omega} - \frac{d\sigma^{\mathrm{PWB}}}{d\Omega}\right), \tag{2.2}$$

where the superscripts B, VAR, and PWB denote first Born, variational, and partial-wave Born. The first term is the (analytical) first Born approximate based on the asymptotic interaction potential [Eq. (2.1)]. The second and third terms in Eq. (2.2) are constructed from elements of the variational and partial-wave Born T matrix, respectively, using elements with $(l, l') \le 2l_{\mathrm{max}}^{\mathrm{ADW}}$. The difference of these terms replaces T-matrix elements with (l, l') in the analytic first Born DCS by corresponding elements of the variational T matrix.

III. IMPLEMENTATION AND RESULTS

Our illustrative case is vibrationally elastic e-CO_2 scattering at and below an incident energy of 1.0 eV. We used the variational FN R matrices of Ref. [16] at C-O separations of $1.9a_0$, $2.0a_0$, $2.1a_0$, $2.1944a_0$, and $2.5a_0$. These variational calculations used small complete active space configuration interaction functions, and allowed for polarization effects and virtual excitation by including in the trial wave function the ground state and all additional configurations predicted to contribute to a Feshbach resonance. The size of the R-matrix box was $r_1 = 10.0a_0$; the maximum partial wave order was $l_{\mathrm{max}}^{\mathrm{VAR}} = 4$. In our calculations, we augmented the variational R matrices via the ADW method to $l_{\mathrm{max}}^{\mathrm{ADW}}$
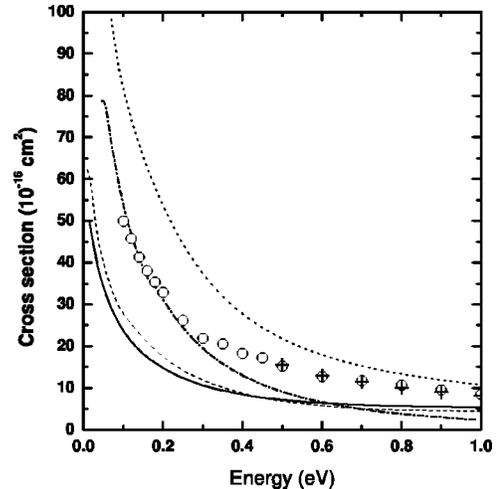

FIG. 1. Integral e-CO_2 cross sections from theoretical calculations using the EMAP method with (dot-dashed line) and without (solid line) DRP corrections. Also shown are theoretical results from the complex Kohn calculations of Rescigno *et al.* [25] (dotted line), the Schwinger multichannel calculations of Ref. [26] (short dashed line), and the experimental data of Ref. [27] (open circles) and Ref. [28] (pluses).
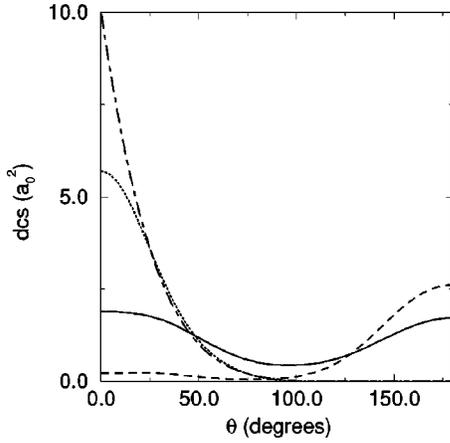
FIG. 2. Theoretical elastic e-CO_2 differential cross sections at 1.0 eV from calculations using only the original variational R matrices of Ref. [16] (long-dashed line), and with the DRP correction (solid line). Also shown are the first Born approximate (dot-dashed line) and the partial-wave Born contribution of Eq. (2.2) (dotted line).

FIG. 3. Total differential cross sections at 1.0 eV from calculations based on the variational R matrices of Ref. [16] (long-dashed line) and with the DRP correction (solid line). Also shown are the experimental results of Gibson *et al.* [23].

$=6$. In the near-target region $r_0 \leq r \leq r_1$ we corrected the polarization response via the DRP as described above. For the effective target radius we chose $r_0 = 5.0 a_0$. For $Q(R)$, $\alpha_0(R)$, and $\alpha_2(R)$, we used the values of Morrison and Hay [17]. The maximum radius of propagation in the external region was $50.0 a_0$.

In Fig. 1 we compare integral cross sections for energies from near-zero to 1 eV to results of measurements and other theoretical calculations. The DRP correction markedly improves the agreement with experiment throughout this energy range. These cross sections are dominated by a virtual-state pole in the Σ_g symmetry [18,19], which renders them especially sensitive to correlation and polarization effects in $0 \leq r \leq r_1$. A measure of this sensitivity is the scattering length. This quantity, which is defined by the limiting slope of the FN eigenphase sum at threshold, can be obtained from a modified extended-range expansion of the K matrix in the limit of zero wave number [20,21]. At equilibrium ($R_{OC} = 2.19440 a_0$), the computed values are $A(\text{VAR}) = -4.44 a_0$ and $A(\text{DRP}) = -8.95 a_0$. (A negative scattering length signifies a virtual state.) The DRP correction brings the scattering length significantly closer to the value $A = -7.2 a_0$ derived from experimental electron-swarm data [22].

Figure 2 shows the effect of the DRP on the 1.0-eV elastic DCS. The variational DCS shows prominent backward but no significant forward scattering, in conflict with experiment [23]. The DRP correction enhances the forward scattering. The resulting improved agreement with experiment is illustrated in Fig. 3. In this figure, the theoretical results incorporate ADW-converged T matrices and Born completion *á la* Eq. (2.2), and are the *total* (vibrationally) elastic cross sections, the sum of the rovibrationally elastic cross section and all rotationally inelastic (but vibrationally elastic) cross sections.
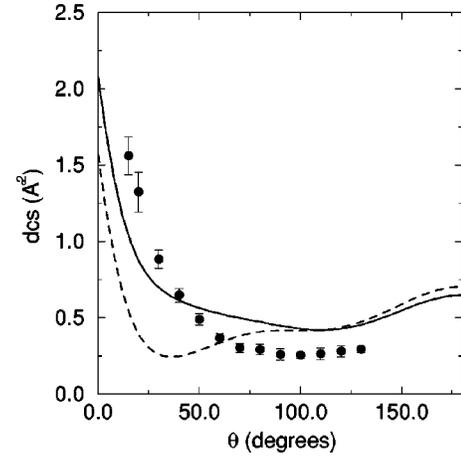
IV. CONCLUSIONS

Two issues require attention in an implementation of the DRP. First, one must choose an effective target radius r_0 that is suitable for the first Born, ADW, and DRP calculations. This choice must be made in the context of the initial variational calculation of the R matrix, so that completeness is assured for $r \leq r_0$. Additionally, static multipole and transition moments should be well defined within r_0. Second, one must choose local external polarization potentials for inward and outward propagation of the R matrix. For outward propagation this argues for the use of polarization pseudostates, computed within r_0 using bound-state methodology [10].

The ADW, DRP, and Born corrections are similarly motivated. All three seek to improve the accuracy of cross sections by improving the representation in the R matrix of the physics outside the target without incurring significant additional computational demands. The DRP offers a simple, systematic solution to a common problem in R-matrix calculations. Such a correction may be especially important for collisions in which polarization response in the near-target region plays a key role: e.g., near the energy of an intermediate- to long-lived resonance and for scattering from highly polarizable targets such as Li_2 [24]. Our results for e-CO_2 scattering at and below 1 eV illustrate the importance of the polarization response and the efficacy of the DRP in correcting both the virtual-state dominated very-low-energy cross section and the forward-scattering dominated DCS's, which, when calculated without the DRP, do not exhibit this important qualitative feature.

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