

Calculation of dissociative attachment of electrons to diatomic molecules by the Schwinger–Lanczos approach

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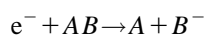
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Numerical studies of resonant scattering of electrons by diatomic molecules with full account of the nonlocal level shift and resonance width operators are carried out with emphasis on the various approximations of the nonlocal potentials. The Schwinger–Lanczos approach proposed recently by Meyer, Horáček and Cederbaum [Phys. Rev. A **43**, 3587 (1991)] is applied and its performance is investigated. The efficiency of the method is further improved by introducing a new local complex potential. Very accurate values of the dissociative attachment cross sections for a *d*-wave resonance model are reported. © 1996 American Institute of Physics. [S0021-9606(96)02520-2]

I. INTRODUCTION

The dissociative attachment process (DA)



and the vibrational excitation (VE) represent the most elementary reaction processes in molecular physics. They are of importance in plasma physics, in physics of planetary atmospheres and outer space,¹ and they can serve as sources of negative ions in discharges, etc. Also their cross sections exhibit sharp threshold peaks and unusual step-like structures (Wigner cups).

Both processes are known to proceed via short-lived electronic states of AB^- . There exist various theoretical descriptions of both processes (see for example Refs. 2 and 3). Here we employ the approach based on the use of the Feshbach projection operators.⁴ The first formulations were due to Chen,⁵ O'Malley⁶ and Bardsley.⁷ Elimination of the electronic degrees of freedom leads to an efficient potential governing the nuclear motion in the short lived electronic states AB^- . This potential is energy dependent, nonlocal and complex. The nonlocality accounts for the fact that the true scattering wave function cannot be factorized into an electronic and a nuclear part, as is assumed in the usual adiabatic or Born–Oppenheimer approximation.

The first exact treatment of the nuclear motion within the nonlocal effective potential was given by Mündel and Domcke⁸ and has been successfully applied to various diatomic molecules (for a recent review see Ref. 2).

Recently Meyer, Horáček and Cederbaum⁹ proposed a very efficient and general method suitable for calculation of DA and VE cross sections—the Schwinger–Lanczos (SL) method. It is the purpose of this paper to test the efficiency of this method and to suggest additional improvements which make the calculation even more efficient.

To calculate DA and VE cross sections two difficulties must be overcome. First, the nonlocal optical potential F must be constructed; as will be shown below this involves the calculation of bound and scattering states of the target

molecule in its ground electronic state. Second, the Lippmann–Schwinger equation involving the nonlocal complex potential F must be solved. In this paper we will address both problems: The first part will be devoted to the calculation of the DA cross section in a simple model⁸ describing a *d*-wave resonance. This model is simple in two respects: it does not exhibit threshold peaks and the contribution from continuum molecular states is negligible. Hence, this model can serve as a first test for any method designed for calculation of DA and VE cross sections. In order to provide a reference calculation we report here very accurate values of DA cross sections for the molecule in three vibrational states. For the construction of the operator F the bound molecular states must be calculated. To find the optimal way of constructing F we tested four discrete variable representation approaches^{10–14}:

- DVR with harmonic oscillator basis,¹⁰
- DVR with Fourier sine-basis,
- DVR with Lanczos basis,⁸
- DVR of Colbert and Miller.¹⁴

The DA cross sections were then calculated by the SL method for a range of incident electron energies and various initial vibrational states of the target molecule and very accurate results were obtained. We estimate that the cross sections are correct to 4–5 figures. The results obtained are compared with the calculation using the exact bound state wave functions.

In the second part of this paper we concentrate on the SL method itself. To test the real power of the SL method we applied it to the calculation of the DA cross section in the system electron–HBr for which a new resonance model was recently proposed by Horáček and Domcke.¹⁵ This system exhibits strong threshold peaks which are very sensitive to minor details of the model and their calculation is very difficult. To make the calculation more efficient and precise we introduce two improvements: First we show how to smooth the oscillations arising in the evaluation of the optical poten-

tial F with the help of the Lanczos σ factors. This smoothing reduces the number of evaluations needed and makes the calculation more stable while keeping the number of Lanczos iterations unchanged. To reduce the number of Lanczos iterations we introduce a new local complex approximation of the potential F . It appears that this local complex potential represents the nonlocal potential F best at the threshold where the calculation is most difficult. The use of this local approximation makes it possible to reduce the number of SL iterations considerably (almost by one order of magnitude at the threshold of HBr DA) allowing thus to calculate very detailed spectra at all energies.

II. RESONANCE MODEL

In the time-independent form of resonant scattering² the motion of the molecule and of the electron is described by the Lippmann–Schwinger equation

$$|\psi_E^{(+)}\rangle = |\varphi_k^{(+)}\rangle|v_i\rangle + (E - H_0 + i\eta)^{-1}V|\psi_E^{(+)}\rangle. \quad (1)$$

Here the double ket notation $|\rangle\rangle$ denotes kets in the combined Hilbert space of electronic and nuclear motion. The Hamiltonian H_0 and the discrete state potential V_d are constructed from a discrete electronic state $|\varphi_d\rangle$ that represents the resonance and the scattering states $|\varphi_k^{(+)}\rangle$ orthogonal to $|\varphi_d\rangle$. We define

$$H_0 = |\varphi_d\rangle[T_N + V_d(R)]\langle\varphi_d| + \int kdkd\Omega_k|\varphi_k^{(+)}\rangle \times \left[T_N + V_0(R) + \frac{1}{2}k^2 \right] \langle\varphi_k^{(+)}|, \quad (2)$$

$$V = \int kdkd\Omega_k|\varphi_d\rangle V_{dk}(R)\langle\varphi_k^{(+)}| + \text{h.c.}, \quad (3)$$

where $V_0(R)$ and $V_d(R)$ denote the potential energies of the target molecule in its ground electronic state and its resonance, respectively and R is the internuclear distance. T_N is the kinetic energy operator of the radial nuclear motion. For calculating DA cross section it is sufficient to consider only the following radial equation describing the nuclear motion in the presence of the resonance²:

$$\langle K^{(-)}| = \langle K| + \langle K^{(-)}|V_{\text{eff}}G_0^{(+)}, \quad (4)$$

where

$$G_0^{(+)} = (E - T_N + i\eta)^{-1} \quad (5)$$

denotes the free Green's function of the nuclear motion and $\langle K|$ the free-particle wave function. The effective interaction V_{eff} is expressed as

$$V_{\text{eff}}(R, R'; E) = V_d(R)\delta(R - R') + F(R, R'; E), \quad (6)$$

where

$$F(R, R'; E) = \int kdkd\Omega_k V_{dk}^*(R) \times G_t^{(+)}\left(R, R'; E - \frac{1}{2}k^2\right) V_{dk}(R'), \quad (7)$$

$V_{dk}(R)$ represents coupling between the discrete state $|\varphi_d\rangle$ and the scattering states $|\varphi_k^{(+)}\rangle$, and $G_t^{(+)}$ is Green's function for the nuclear motion in the target electronic state

$$G_t^{(+)}(R, R'; E) = \langle R|(E - T_N - V_0 + i\eta)^{-1}|R'\rangle. \quad (8)$$

The effective interaction V_{eff} is nonlocal, complex and energy dependent. The scattering amplitude for the dissociative attachment is given in terms of $\langle K^{(-)}|$ as follows:

$$T_{\text{DA}} = \langle K^{(-)}|V_{dk_i}|v_i\rangle, \quad (9)$$

where v_i denotes the initial vibrational state of the target. Hence the complicated many-body problem is reduced to solving one radial Lippmann–Schwinger equation Eq. (4) describing the motion of the nuclei in the resonance state. This enormous simplification follows from the assumption that only one discrete state $|\varphi_d\rangle$ contributes to this process. All the complexity of the resonant process is therefore concentrated in the nonlocal operator $F(R, R'; E)$ and in solving Eq. (4).

III. SCHWINGER–LANCZOS APPROACH

Since the Schwinger–Lanczos method was discussed in detail in Ref. 9 we give here only a brief description of it. Let us start with the Lippmann–Schwinger equation

$$|\varphi\rangle = |u\rangle + G_0U|\varphi\rangle, \quad (10)$$

where $|u\rangle$ and G_0 are the solution and the Green's function of some zero order Hamiltonian, H_0 , and $|\varphi\rangle$ denotes the solution of the full Hamiltonian $H = H_0 + U$. In the SL approach a non-orthogonal basis set of vectors is defined as follows:

$$|g_1\rangle = |u\rangle\langle u|U|u\rangle^{-1/2}, \quad (11)$$

$$\beta_i|g_{i+1}\rangle = G_0U|g_i\rangle - \alpha_i|g_i\rangle - \beta_{i-1}|g_{i-1}\rangle, \quad (12)$$

or explicitly

$$|r_i\rangle = G_0U|g_i\rangle - \beta_{i-1}|g_{i-1}\rangle, \quad (13)$$

$$\alpha_i = \langle g_i|U|r_i\rangle, \quad (14)$$

$$|s_i\rangle = |r_i\rangle - \alpha_i|g_i\rangle, \quad (15)$$

$$\beta_i = \langle s_i|U|s_i\rangle^{1/2}, \quad (16)$$

$$|g_{i+1}\rangle = \beta_i^{-1}|s_i\rangle, \quad (17)$$

which diagonalize U and tridiagonalize UG_0U :

$$\langle g_i|U|g_j\rangle = \delta_{ij}, \quad (18)$$

$$\langle g_i|UG_0U|g_{i-1}\rangle = \beta_{i-1}, \quad (19)$$

$$\langle g_i|UG_0U|g_i\rangle = \alpha_i, \quad (20)$$

$$\langle g_i|UG_0U|g_{i+1}\rangle = \beta_i, \quad (21)$$

$$\langle g_i | U G_0 U | g_j \rangle = 0 \quad \text{if } |i-j| > 1. \quad (22)$$

Since G_0 as well as $U G_0 U$ are complex symmetric operators (non-hermitian) one has to use the complex symmetric scalar product, i.e., the scalar product in the above equations is defined as

$$\langle u | v \rangle = \int_0^\infty u(r) v(r) dr. \quad (23)$$

Once the vectors $|g_i\rangle$ are constructed, the solution $|\varphi\rangle$ may be written as

$$|\varphi\rangle = \sum_{i=1}^L a_i |g_i\rangle, \quad (24)$$

where the coefficients a_i are given by simple algebraic relations in terms of α_i and β_i .⁹ The SL approach is iterative and requires no explicit inversion of a matrix. In what follows the number of Lanczos steps will be referred to as L .

IV. CALCULATION OF THE OPTICAL POTENTIAL F

The nonlocal complex energy dependent potential F describing the motion of the nuclei in the presence of a short lived state is defined as^{2,8}

$$F(R, R'; E) = \int_0^\infty dE' V_{E'}(R) \times (E - H_0 - E' + i\eta)^{-1} V_{E'}(R'), \quad (25)$$

where we have replaced V_{dk} by its angle-integrated value V_{E^2} and where H_0 is the Hamiltonian of the target molecule in its ground electronic state

$$H_0 = -\frac{\hbar^2}{2M} \frac{d^2}{dR^2} + V_0(R). \quad (26)$$

The common way of evaluation for integrals of this type consists in introducing eigenstates of the operator H_0 , i.e.,

$$H_0 |n\rangle = E_n |n\rangle \quad (27)$$

and representing Eq. (25) in the form

$$F|\psi\rangle = \sum_n \int \int dE' V_{E'}(R) \times \frac{|n\rangle\langle n|}{E - E_n - E' + i\eta} V_{E'}(R') \psi(R') dR', \quad (28)$$

where we sum over discrete states of the Hamiltonian H_0 and integrate over continuum states. Separating real and imaginary parts by writing $F = \Delta - (i/2)\Gamma$ we arrive at

$$\Delta(R, R'; E) = \sum_n P \int_0^\infty dE' V_{E'}(R) \times \frac{|n\rangle\langle n|}{E - E_n - E'} V_{E'}(R'), \quad (29)$$

$$\Gamma(R, R'; E) = 2\pi \sum_n V_{E-E_n}(R) |n\rangle\langle n| V_{E-E_n}(R'). \quad (30)$$

In order to make the evaluation of Eqs. (29) and (30) possible we diagonalize H_0 in a basis set $\{\phi_n(R)\}_{n=1}^M$ of square integrable functions. The continuum states are thus discretized and the integrals in Eqs. (29) and (30) replaced by sums. The number M depends on the choice of the basis set and must be large enough to provide good approximations to the eigenstates $|n\rangle$ and energies E_n . Various choices of the basis sets $\{\phi_n\}$ will be discussed in the next section. The sums in Eqs. (29) and (30) will be truncated and the operators Δ and Γ explicitly expressed as

$$\Delta(R, R'; E) = \sum_{n=1}^N P \int_0^\infty dE' V_{E'}(R) \times \frac{\langle R|n\rangle\langle n|R'\rangle}{E - E_n - E'} V_{E'}(R'), \quad (31)$$

$$\Gamma(R, R'; E) = 2\pi \sum_{n=1}^N V_{E-E_n}(R) \langle R|n\rangle \times \langle n|R'\rangle V_{E-E_n}(R'). \quad (32)$$

The principal value integration, that appears in Eq. (31), is cumbersome. In order to be able to do it once for all we assume $V_E(R)$ to be of the product form

$$V_E(R) = g(R) f(E) \quad (33)$$

and define

$$\Gamma(E) = 2\pi f^2(E), \quad (34)$$

$$\Delta(E) = \int_0^E dE' \frac{f^2(E')}{E - E'}. \quad (35)$$

Hence we arrive at

$$\Delta(R, R'; E) = \sum_{n=1}^N g(R) \langle R|n\rangle \Delta(E - E_n) \langle n|R'\rangle g(R'), \quad (36)$$

$$\Gamma(R, R'; E) = \sum_{n=1}^N g(R) \langle R|n\rangle \Gamma(E - E_n) \langle n|R'\rangle g(R'). \quad (37)$$

The number of terms needed for the sums (36) and (37) to converge depends on the incident electron energy and varies from molecule to molecule. For example in the d -wave model discussed here the true bound states alone represent F accurately and the contribution from the continuum states is negligible. This is however not true in general. In some cases the contribution from the continuum part of the spectrum of H_0 is essential (e.g., H_2).¹⁶

V. TEST CALCULATIONS

A. d -wave resonance model

As a first test we apply the SL method to the calculation of DA cross section using a model proposed by Mündel and

TABLE I. Comparison of the DVR methods.

Method	DVR dimension	Time requirement
Exact Morse solution	25	100%
DVR of Colbert and Miller	300	105%
DVR with Fourier sine-basis	50	130%
DVR with Lanczos basis	30	380%
DVR with LHO functions	50	650%

Domcke.⁸ This model describes a d -wave resonance and serves as a standard example for testing various approaches designed for the calculation of resonance scattering. The model is defined as follows:

$$V_0(R) = D_0(e^{-2\alpha_0(R-R_0)} - 2e^{-\alpha_0(R-R_0)}) + Q_0, \quad (38)$$

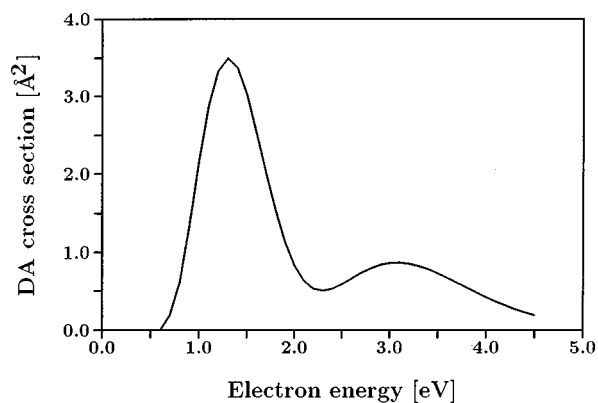
$$V_d(R) = D_1(e^{-2\alpha_1(R-R_0)} - 2t_1e^{-\alpha_1(R-R_0)}) + Q_1, \quad (39)$$

$$\Gamma(E) = A(E/B)^\alpha e^{-E/B}, \quad (40)$$

$$g(R) = e^{-C(R+1/(2\sqrt{C}))^2}. \quad (41)$$

Here $D_0=5$ eV, $D_1=3.2$ eV, $t_1=0.2$, $\alpha_0=\alpha_1=1.96$ Å⁻¹, $A=1.757$ eV, $B=1.667$ eV, $C=0.98$ Å⁻², $\alpha=2.5$, $Q_0=5$ eV, $Q_1=1.2$ eV and $\mu=1$ a.u. The main input for the calculation is the optical potential F given by Eq. (25). To test the efficiency of the calculation of F we performed a series of calculations with various DVR bases and compared the results with the one obtained using the exact bound state functions of the Morse potential as a basis set. In all the calculations the bound state wave functions were calculated in the form of sums of the respective basis functions. (For details see the Appendix.) Since in our scattering calculation we use an optimized non-equidistant grid it is of great practical significance to have a general analytic expression for the vibrational wave functions of the molecular ground state. When the wave functions are known only at a set of points (for example DVR points) an interpolation between these points must be performed. This introduces additional errors and decreases the stability of the calculation.

We used four different DVR bases in our calculations (for definitions see the Appendix): harmonic oscillator

FIG. 2. The same as Figure 1 but the target was initially excited to $\nu=1$.

functions,¹⁰ Fourier sine-basis, Lanczos basis⁸ and the DVR of Colbert and Miller.¹⁴ The number M of terms needed for the DA cross section to converge was tested. Eventually all DVR techniques converged with increasing M but M was different for different DVRs. This is shown in Table I, where the time of computation is shown together with the number of terms M (dimension of DVR space). We see that for example 50 harmonic oscillator states are needed to arrive at the same accuracy as is obtained with 30 states using the Lanczos basis or 300 states using the method of Colbert and Miller. It is evident from the Table I that the DVR method of Colbert and Miller¹⁴ is fastest but simultaneously requires a large number (hundreds) of basis states. Next in speed is the method employing Fourier sine-basis functions which requires only a little longer time than the Colbert and Miller approach. However, the difference in M is very significant. We need only 50 states to obtain the same accuracy. All our experience indicates that the Fourier sine-basis set represents a very efficient, stable, robust and accurate means for the calculation of the optical potential F . All results referred to in this paper were obtained with this basis.

Once the optical potential F is constructed the SL method can be used and the DA cross section calculated.

The energy dependence of the calculated DA cross section for three initial vibrational states $\nu=0, 1$ and 2 is shown

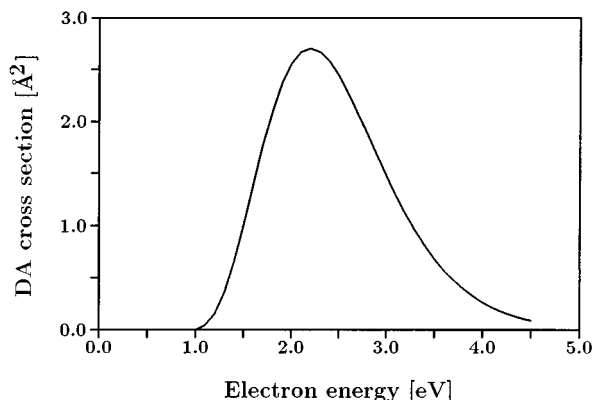
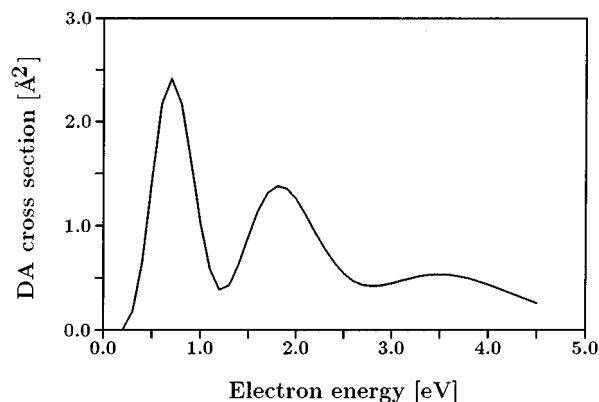
FIG. 1. DA cross section for the molecule in the ground vibrational state for the d -wave resonance model of Münder and Domcke (Ref. 8).FIG. 3. The same as Figure 1 but for $\nu=2$.

TABLE II. DA cross section for different vibrational states.

Electron energy [eV]	DA cross section [\AA^2], initial vibrational state		
	$v=0$	$v=1$	$v=2$
0.3	0.1818
0.4	0.6592
0.5	1.4517
0.6	2.1682
0.7	...	0.1922	2.4149
0.8	...	0.6094	2.1683
0.9	...	1.3287	1.6260
1.0	...	2.1607	1.0316
1.1	0.0455	2.8662	0.5869
1.2	0.1521	3.3271	0.3896
1.3	0.3607	3.4952	0.4301
1.4	0.6582	3.3711	0.6323
1.5	1.0099	3.0214	0.8986
1.6	1.3890	2.5435	1.1442
1.7	1.7637	2.0262	1.3127
1.8	2.0970	1.5402	1.3811
1.9	2.3649	1.1339	1.3538
2.0	2.5578	0.8306	1.2516
2.1	2.6699	0.6329	1.1036
2.2	2.7033	0.5298	0.9385
2.3	2.6672	0.5024	0.7799
2.4	2.5736	0.5285	0.6442
2.5	2.4347	0.5869	0.5403
2.6	2.2638	0.6592	0.4707
2.7	2.0729	0.7309	0.4329
2.8	1.8720	0.7921	0.4214
2.9	1.6698	0.8365	0.4290
3.0	1.4726	0.8612	0.4485
3.1	1.2855	0.8658	0.4733
3.2	1.1116	0.8518	0.4977
3.3	0.9529	0.8217	0.5177
3.4	0.8103	0.7788	0.5305
3.5	0.6838	0.7265	0.5347
3.6	0.5729	0.6679	0.5299
3.7	0.4768	0.6058	0.5166
3.8	0.3943	0.5427	0.4959
3.9	0.3241	0.4808	0.4690
4.0	0.2648	0.4213	0.4375
4.1	0.2152	0.3656	0.4031
4.2	0.1739	0.3145	0.3669
4.3	0.1398	0.2682	0.3303
4.4	0.1118	0.2270	0.2942
4.5	0.0890	0.1907	0.2596

in Figures 1–3 and summarized in Table II. All the results were obtained by solving the LS equation in coordinate representation on an optimized grid (for details of the calculation see Refs. 17 and 18). To obtain the required high accuracy of the calculated cross sections the Romberg extrapolation technique proposed by Horáček was employed.¹⁷ The results are assumed to be correct to all figures shown in the table.

B. Acceleration of SL iterations

The d -wave resonance model discussed in the previous section is simple in the sense that the number N of terms needed for the evaluation of the optical potential F , Eqs. (31) and (32), is low and therefore the number of steps required

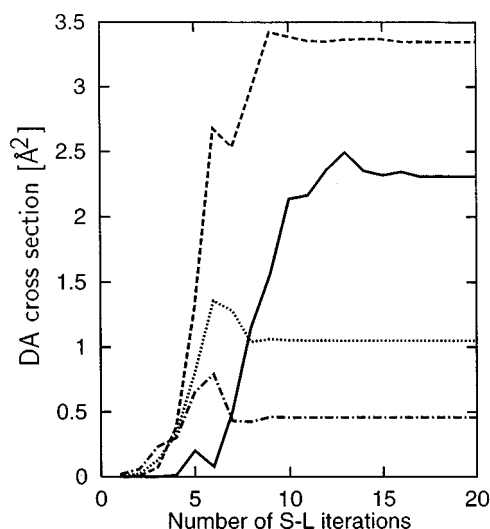


FIG. 4. DA cross section for the HBr resonance model (Ref. 15) plotted against the number of SL iterations at various electron energies: solid line—0.4 eV, dashed line—0.6 eV, dotted line—0.8 eV and dash-dotted line—1.0 eV.

by the SL method to converge is low too. However, this is not true in general; for example for the calculation of DA in H_2 or in polar molecules such as HCl and HBr the number of terms is high and consequently the number of SL steps also increases.^{8,16}

Here we apply the SL method to the calculation of DA cross section in the system electron-HBr for which a new model was recently proposed by Horáček and Domcke.¹⁵ This model being a modification of the HCl model of Münder and Domcke⁸ is defined as follows:

$$V_0(R) = D_0(e^{-2\alpha_0(R-R_0)} - 2e^{-\alpha_0(R-R_0)}) \quad (42)$$

with $D_0 = 3.92$ eV, $\alpha_0 = 0.96$ a.u.⁻¹ and $R_0 = 2.67$ a.u.,

$$V_d(R) = D_1 e^{-2\alpha_1(R-R_0)} + Q_1, \quad (43)$$

$$\Gamma(E) = A(E/B)^\alpha e^{-E/B}, \quad (44)$$

$$g(R) = e^{-C(R-R_0)}. \quad (45)$$

For large values of R ($R > R_1$) the function $g(R)$ is modified as¹⁵

$$g(R) = e^{-C(R-R_0)} e^{-D(R-R_1)}. \quad (46)$$

The parameters of the model are: $D_1 = 1.736$ eV, $\alpha_1 = 0.9871$ a.u.⁻¹, $Q_1 = 0.56$ eV, $A = 4.039$ eV, $B = 4.615$ eV, $C = 0.1176$ a.u.⁻¹, $R_1 = 2.9$ a.u. and $D = 0.4$ a.u.⁻¹

The number of iterations needed for the SL approach to converge depends (for fixed parameters of the model) on the energy of incident electrons. This is seen in Figure 4 which shows DA cross sections calculated with the HBr model described above for various incident electron energies: the solid line corresponds to the energy $E = 0.4$ eV which lies just above the threshold for DA ($E_{th} = 0.397$ eV); the rate of convergence increases with increasing energy: $E = 0.6$ eV—dashed line, $E = 0.8$ eV—dotted line and $E = 1.0$ eV—dash-dotted line.

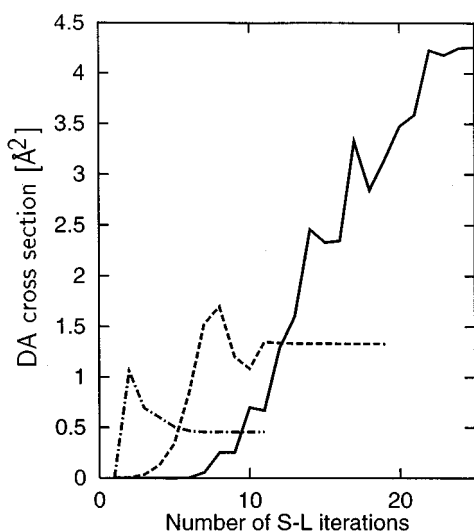


FIG. 5. DA cross section for the modified HBr resonance model (Ref. 15) [D in Eq. (46) reduced to 0.2 a.u.^{-1}] at three electron energies: solid line— 0.4 eV , dashed line— 0.75 eV and dash-dotted line— 1.0 eV .

Generally it is difficult to predict the rate of convergence of the SL method. Changing slightly the parameters of the model may have a great influence on the convergence. To see this we show in Figure 5 the DA cross sections obtained with the HBr model discussed above in which the value D is reduced from 0.4 to 0.2 a.u.^{-1} . This change has only marginal effect on the optical potential F and keeps the DA cross section essentially unchanged for higher energies (it modifies the long range behavior of F only) but it has a strong influence in the threshold region. The convergence in the threshold region ($E=0.4 \text{ eV}$ —solid line) is now very slow.

It is of vital importance to keep the number of SL iterations [i.e., the number of terms in Eq. (24)] as low as possible. This is not only because the computation time increases with increasing number of terms (for treating more complicated molecules we need the calculation to be as fast as possible). There is a deeper reason. The Lanczos algorithm is known to become numerically unstable when the first Ritz-vector converges.¹⁹ After a certain number of iterations the orthonormality relation (18) will be disobeyed. This obstacle can be overcome by explicit reorthonormalization, but this is an expensive process because all previous Lanczos vectors have to be stored.

The most difficult part in calculations of the dissociative and vibrational cross sections is the calculation in the threshold region. If the energy E is just above the threshold a large number of terms in the effective potential F contribute and F is a “strong” operator. As a result a large number of SL iterations must be performed and this involves a large number of meshpoints.

To avoid this problem we introduce a local complex energy-dependent potential V_L which approximates the non-local potential F at the threshold. This can be done as follows: Generally our problem is to solve the LS equation

$$|\varphi\rangle = |u\rangle + G_0(E)(V_d + F)|\varphi\rangle, \quad (47)$$

where V_d is the local potential of the discrete state and F is a complicated nonlocal complex energy-dependent potential given by Eq. (7). As is well known,^{20,17} it is easy to solve the LS equation with local interactions. A much more difficult problem is to treat the nonlocal potential F . Let us assume that the LS equation was solved taking into account only the local potential V_d . Then we get

$$|\varphi\rangle = (1 - G_0 V_d)^{-1} |u\rangle + G F |\varphi\rangle, \quad (48)$$

where

$$G = (1 - G_0 V_d)^{-1} G_0. \quad (49)$$

The operator F is an integral operator

$$F|\varphi\rangle = \int F(x, x') \varphi(x') dx'. \quad (50)$$

A well known²¹ local approximation for F can be obtained by expanding the wave function $\varphi(x')$ in the Taylor series around a point x

$$F|\varphi\rangle = \int F(x, x') (\varphi(x) + (x' - x) \varphi'(x) + (x' - x)^2 / 2 \varphi''(x) + \dots) \quad (51)$$

and keeping only the first term in this expansion

$$F|\varphi\rangle \sim \int F(x, x') dx' \varphi(x) = V_L(x) \varphi(x). \quad (52)$$

This local approximation for F approximates the action of F on $\varphi(x)$ well only if the wave function φ does not change much with x , so that the higher terms in the expansion (51) can be neglected. The approximation (52) is essentially a low energy approximation and can be expected to perform well in the close vicinity of the threshold. This feature is of great practical value because the DA and VE cross sections exhibit threshold peaks and it is very difficult task to get an accurate value of the cross section at the threshold.

Once the local complex potential V_L is known it can be added to the discrete state potential V_d and the LS equation may be written in the form

$$|\varphi\rangle = (1 - G_0(V_d + V_L))^{-1} |u\rangle + G(F - V_L)|\varphi\rangle, \quad (53)$$

where

$$G = (1 - G_0(V_d + V_L))^{-1} G_0. \quad (54)$$

Since the local potential V_L approximates F the operator $G(F - V_L)$ is much “weaker” than the original operator GF and as a result a much lower number of SL iterations is needed to get converged results.

To see the effect of the introduction of the local complex potential V_L on the rate of convergence of the SL method we introduce a parameter λ and apply the SL method to the operator $F - \lambda V_L$. For $\lambda = 0$ there is no subtraction and we have the original problem whereas for $\lambda = 1$ the full potential V_L is subtracted. The results are in Figure 6. The dashed line shows the DA cross sections calculated at the energy $E = 0.4 \text{ eV}$, i.e., very close to the DA threshold for $\lambda = 0$; the dotted line corresponds to partially subtracted potential, $\lambda = 0.5$, the

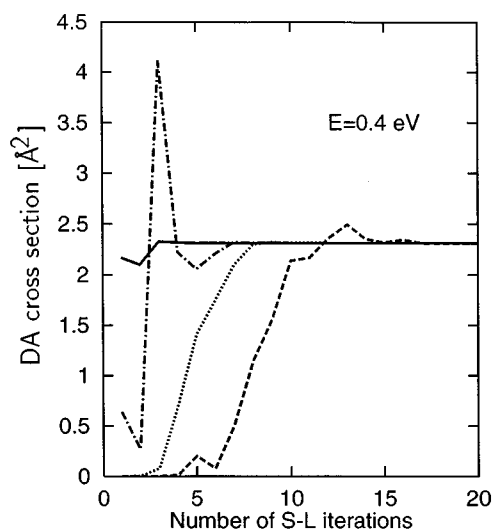


FIG. 6. DA cross section for the HBr resonance model (Ref. 15) at the energy $E=0.4$ eV and for various degrees of subtraction of the local potential V_L . The calculations were carried out for the operator $F-\lambda V_L$. The solid line corresponds to the full subtraction, $\lambda=1$ whereas the dashed line was obtained with no subtraction, $\lambda=0$. The dotted line corresponds to $\lambda=0.5$ and the dash-dotted line to $\lambda=1.2$.

dash-dotted line corresponds to $\lambda=1.2$ and finally the solid line shows the results obtained for $\lambda=1$. The improvement in the convergence rate is impressive. Three SL iterations only are enough to yield the DA cross section with an accuracy exceeding the accuracy of the best experiments.

We subjected our approach to an even more difficult test. We have calculated the DA cross sections for the modified HBr model [D in Eq. (46) is reduced to 0.2]. The solid line in Fig. 7 shows the calculated DA cross section for $E=0.4$ eV for $\lambda=1$ —full subtraction, the dashed line follows from $\lambda=0.5$ —partial subtraction and the dash-dotted line was obtained without any subtraction, $\lambda=0$. Even in this case we

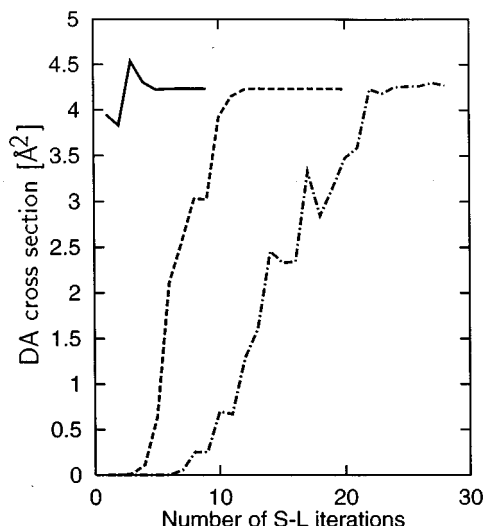


FIG. 7. The same as Figure 6 but for the modified HBr model. Solid line, $\lambda=1$, full subtraction, dashed line, $\lambda=0.5$, partial subtraction and the dash-dotted line was obtained without any subtraction, $\lambda=0$.

see that 4–5 terms give very accurate results and the number of iterations needed is reduced almost by one order of magnitude. Similar behavior is observed also at somewhat higher energies. Hence, the use of the local complex potential not only makes the calculation faster and more stable but also allows to get accurate results in cases in which the number of iterations is so large that the Lanczos scheme breaks down.

VI. LANCZOS SIGMA FACTORS

In this section we concentrate on the behavior of the DA cross section at an increasing number of terms in Eqs. (36) and (37). The sums are in principle infinite because the continuum states also contribute to F . It is commonly accepted to approximate the integral over the continuum states by a finite sum of discrete terms. It appears that for many diatomic molecules this is a very good approximation and converged results are obtained with a very limited number of continuum terms. However, the convergence is usually erratic and oscillatory. Such oscillations are common phenomena in many other problems. A typical example is the well known Gibbs phenomenon. A very efficient way to remove the oscillations was suggested by Lanczos.²² This approach consists in the following. Generally our potential F is of the form

$$F = \sum_{n=1}^N g(R) b_n(R) (\Delta(E - E_n) - i/2\Gamma(E - E_n)) b_n(R') g(R'), \quad (55)$$

where $\{b_n(R)\}$ are eigenfunctions of the target molecular Hamiltonian H_0 , Eq. (26), and $g(R)$ describes the R -dependence of the coupling term $V_E(R)$. According to Lanczos²² we replace Eq. (55) by

$$F = \sum_{n=1}^N g(R) b_n(R) \sigma_n^N (\Delta(E - E_n) - i/2\Gamma(E - E_n)) \sigma_n^N b_n(R') g(R'), \quad (56)$$

where

$$\sigma_n^N = \frac{1 - \exp\{-[\alpha(n - N + 2)/(N + 1)]^2\}}{1 - \exp(-\alpha^2)}. \quad (57)$$

The only difference between Eqs. (55) and (56) is the presence of numerical factors, σ_n^N . The parameter α is a free parameter which is to be chosen by trial and error. Luckily, there exists a broad range of values of α , to a large extent independent of the energy, for which the introduction of σ_n^N improves the convergence.²³ In Fig. 8 we compare DA cross section calculated with $\alpha=5$ (solid line) with that obtained with no use of Lanczos sigma factors (dashed line) at two energies in the threshold region, $E=0.45$ eV and $E=0.60$ eV. The smoothing effect is obvious. It appears that the introduction of the Lanczos σ factors makes the convergence smoother and much more monotonic except for a very narrow energy-range in the close vicinity of the threshold.

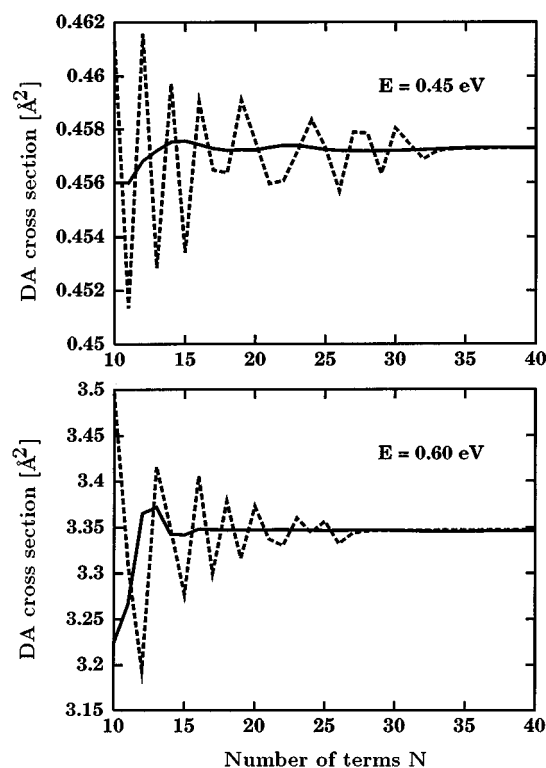


FIG. 8. DA cross section for the HBr resonance model at two electron energies, $E=0.45$ eV, $E=0.60$ eV plotted versus the number N of states in the expansion (55) showing the smoothing effect of the Lanczos σ -factors, Eq. (57). The solid line was smoothed with $\alpha=5$ whereas the dashed line was obtained without smoothing.

This smoothing allows to reduce the number N in expansion (56) and consequently increases the accuracy and stability of our calculation.

VII. CONCLUSION

The purpose of this paper was to study the performance of the Schwinger–Lanczos method as applied to the calculation of the DA cross sections in the resonance nonlocal model. As a first step in this calculation the optical potential F , Eq. (25), must be constructed. This is achieved by diagonalizing the Hamiltonian H_0 , Eq. (28), in a basis of square integrable functions. We tested four DVR bases $\{\phi_n\}$ and the calculated DA cross sections were compared with those obtained with the exact (Morse) bound state functions. It was shown that among all four DVR bases studied here the Fourier sine-basis performs best. The calculation within this basis set is very fast, stable, accurate and does not require a large number of basis functions.

Using this basis set we calculated very accurate (4–5 digits) values of the DA cross section for the d -wave resonance model⁸ for three initial vibrational states of the target molecule ($v=0, 1$ and 2). The cross sections can be found in Table II.

It appears that the convergence of the Schwinger–Lanczos approach is very fast in this case and a very small number L of Lanczos iterations ($L < 10$) yields converged re-

sults. However, for realistic models describing the molecules such as H_2 , HCl , HBr , DBr , etc., the convergence is much slower. To increase the convergence rate of the Schwinger–Lanczos method a local approximation for the nonlocal potential F is proposed. It was shown that the introduction of this local approximation reduces the number of SL terms considerably and makes the calculation very efficient even in the worst cases.

Finally, the Lanczos sigma factors were introduced in order to make the calculation of the optical potential more monotonic and stable.

Summarizing we can say that the Schwinger–Lanczos approach yields a very efficient and stable method of calculating DA cross sections in diatomic molecules. Extension to the treatment of polyatomic molecules is under study.

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APPENDIX

For completeness of the presentation we give here explicit DVR formulas used throughout this paper.

1. DVR with harmonic oscillator functions (Ref. 10)

This method is derived from the solution of the Schrödinger equation with the quadratic potential function $V(x) = a(x-b)^2$. The wave functions

$$\phi_k(z) = \left[\frac{c}{\sqrt{\pi} 2^k k!} \right]^{1/2} e^{-z^2/2} H_k(z), \quad k=0, 1, \dots,$$

where

$$c = \left[\frac{2\mu a}{\hbar^2} \right]^{1/4}, \quad z = c(x-b),$$

$H_k(z)$ is the standard Hermite polynomial²⁴ and μ is the reduced mass, are used as the basis set for the DVR. The matrix elements of the (scaled) position operator Z and of the kinetic energy T are

$$Z_{i,i-1} = \left[\frac{i}{2} \right]^{1/2},$$

$$T_{i,i} = \sqrt{\frac{a\hbar^2}{2\mu}} \left(i + \frac{1}{2} \right),$$

$$T_{i,i+2} = -\frac{1}{2} \sqrt{\frac{a\hbar^2}{2\mu}} [(i+1)(i+2)]^{1/2}$$

(all the matrices are symmetric).

2. DVR with Fourier sine-basis

The Fourier sine-basis is defined only on the interval (a, b) so we have to suppose that $V(x) \rightarrow \infty$ for $x \notin (a, b)$ and the solution is also restricted to a suitably chosen interval (a, b) . The basis is composed of the functions

$$\phi_k(x) = \left[\frac{2}{b-a} \right]^{1/2} \sin \frac{k\pi(x-a)}{b-a}, \quad k=1, 2, \dots$$

and the non-zero matrix elements of the position operator X and the kinetic energy T are

$$X_{i+j, i} = -\frac{8ij(b-a)}{\pi^2(i+j)^2(i-j)^2}, \quad T_{i,i} = \frac{\hbar^2}{2\mu} \left[\frac{i\pi}{b-a} \right]^2.$$

3. DVR of Colbert and Miller (Ref. 14)

In contrast to the previous case where k was always finite, the infinite order limit was taken into account in this method. Its advantages are equally spaced grid points and a uniform and simple kinetic energy matrix. Consider for example one Cartesian dimension, $-\infty < x < \infty$ and DVR points $\{x_i\}$ defined as

$$x_i = i\Delta x, \quad i=0, \pm 1, \pm 2, \dots$$

Then, for the DVR representation of the kinetic energy one obtains

$$T_{i,j} = \frac{\hbar^2}{2\mu\Delta x^2} (-1)^{i-j} \begin{cases} \pi^2/3 & i=j \\ 2/(i-j)^2 & i \neq j \end{cases}.$$

4. DVR with Morse–Lanczos basis (Ref. 8)

The Morse–Lanczos basis represents a very efficient tool for solving Morse-like problems via DVR. This four-parameter basis (D, α, x_0 are obtained from the Morse potential and γ is an arbitrary parameter greater than $-1/2$) is based on the associated Laguerre polynomials $L_k^{(\alpha)}(z)$ ²⁴

$$\phi_k(z) = \left[\frac{\alpha k!}{\Gamma(2\gamma + k + 1)} \right]^{1/2} z^{\gamma+1/2} e^{-z/2} L_k^{(2\gamma)}(z),$$

$$k=0, 1, \dots,$$

where

$$z = 2\delta e^{-\alpha(x-x_0)}, \quad \delta = \frac{\sqrt{2\mu D}}{\alpha\hbar}.$$

The Morse–Lanczos basis set is complete and tridiagonalizes the Morse Hamiltonian. The non-zero matrix elements of the position operator and the kinetic energy are

$$Z_{i,i} = 2i + 2\gamma + 1, \quad Z_{i,i-1} = -\sqrt{i(i+2\gamma)},$$

$$T_{i,i} = \frac{1}{4} \frac{\alpha^2 \hbar^2}{2\mu} (2i(i+2\gamma+1) + 2\gamma+1),$$

$$T_{i,i+2} = -\frac{1}{4} \frac{\alpha^2 \hbar^2}{2\mu} \times \sqrt{(i+2)(i+1)(i+2\gamma+2)(i+2\gamma+1)}.$$

5. Exact Morse functions

The Morse potential²⁵

$$V(x) = D(e^{-2\alpha(x-x_0)} - 2e^{-\alpha(x-x_0)}),$$

describes quite accurately the potential curve of many diatomic molecules. The Schrödinger equation for this potential is exactly solvable and the corresponding bound state wave functions and energy levels can be written in the form

$$\psi_k(z) = \left[\frac{a\alpha k!}{\Gamma(a+k+1)} \right]^{1/2} z^{a/2} e^{-z/2} L_k^{(a)}(z),$$

$$E_k = -\frac{a^2 \alpha^2 \hbar^2}{8\mu},$$

where

$$z = 2\delta e^{-\alpha(x-x_0)}, \quad a = 2(\delta - k) - 1, \quad \delta = \frac{\sqrt{2\mu D}}{\alpha\hbar}.$$

[To treat the problem correctly, we have to solve the radial equation with the boundary conditions $\psi(0)=0$ and $\psi(x) \rightarrow 0$ for $x \rightarrow \infty$. It is difficult to impose the condition in $x=0$ so the equation is usually solved on the whole interval $(-\infty, \infty)$. Because of the repulsive potential barrier this solution is practically equal to zero for $x=0$ and therefore is expected to be very close to the true one.]

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