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Electron-molecule scattering treated with the use of separable approximations for the nonlocal part of the interaction: Static exchange calculations for $e^- + H_2$ and $e^- + N_2$

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We have formulated and applied a method for solving the low-energy electron-molecule collision problem. This method treats the scattering by the local and nonlocal parts of the interaction differently. A differential equation method is used to obtain a solution of the set of coupled equations which describe the scattering by the (nonspherical) local potential. The T-matrix expansion method is used to account for the scattering by the nonlocal part of the interaction. The method is tested by application to low-energy e^--H_2 and e^--N_2 scattering in the static exchange approximation.

I. INTRODUCTION

The scattering by a local potential is considerably simpler to treat numerically than the scattering by a nonlocal interaction. The development of model potentials treating the nonlocal exchange and correlation interaction with a local approximation was therefore an important step towards the solution of the elastic electron-molecule scattering problem.[1–4] However, although the exchange correlation model potential may be parameter-free we hesitate to call it an *ab initio* potential. An *ab initio* theory must account for the nonlocal character of the interaction. Basis-set approaches[5]—e.g., the T-matrix expansion method,[6] the Schwinger variational method,[7] the R-matrix method,[8] and the Kohn method[9]—are tools to achieve this purpose. However, basis-set expansion methods are fairly elaborate computationally if one wants to achieve a high degree of accuracy. A convenient way to solve the electron-molecule scattering problem is to take advantage of the fact that part of the interaction is local and to account for the local and nonlocal interactions by different methods. This route was recently taken by several investigators.[10–13]

Adopting a one-electron picture for the description of the elastic scattering process in the fixed-nuclei limit, one finds that the scattering is determined by the effective Hamiltonian

$$H_{\mathrm{eff}} = T + U \ , \tag{1.1}$$

where T denotes the kinetic energy of the scattered electron and U denotes the optical potential. The optical potential can be obtained by projecting the full potential on the elastic channel.[14] We prefer to take the alternative route and identify, following Bell and Squires,[15] the optical potential with the mass operator of the one-particle Green's function. The mass operator can be evaluated by using many-body perturbation theory. One of the advantages of this approach is that target correlations are automatically included in a balanced way.

The optical potential U can be split into a local and a nonlocal term,

$$U(\mathbf{r},\mathbf{r}',E) = V(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + W(\mathbf{r},\mathbf{r}',E) \tag{1.2}$$

[to be precise, $U(\mathbf{r},\mathbf{r}')$ and $W(\mathbf{r},\mathbf{r}')$ which appear in Eqs. (1.2) and (1.4) denote the integral kernels of the interaction operators U and W, respectively]. The local potential $V(r)$ is real, energy independent, and long ranged, whereas the nonlocal potential W is short ranged. It is, however, in general energy dependent and becomes complex above the first inelastic threshold. In the static exchange approximation—the simplest useful approximation to U—the local potential V becomes the static interaction

$$V(\mathbf{r}) = 2\sum_j \int dr' \frac{|\phi_j(\mathbf{r}')|^2}{|\mathbf{r}-\mathbf{r}'|} - \sum_k \frac{z_k}{|\mathbf{r}-\mathbf{R}_k|} \ , \tag{1.3}$$

and W becomes the exchange interaction

$$W(\mathbf{r},\mathbf{r}') = -\sum_j \frac{\phi_j(\mathbf{r})\phi_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \ . \tag{1.4}$$

In the above equations $\{\phi_j\}$ denotes the set of doubly occupied self-consistent-field (SCF) orbitals, $\{\mathbf{R}_k\}$ and $\{z_k\}$ denote the sets of nuclear positions and charges, respectively. Moreover, a closed-shell target molecule is assumed for simplicity and atomic units are used throughout. Considering the exact optical potential, on the other hand, one finds that the local potential V contains the static interaction with the fully correlated (but "frozen") target, as well as the long-range part of the polarization potential. The nonlocal potential W now does not only contain all exchange interactions, it also contains the nonlocal part of that interaction which is due to the virtual excitation of the target by the projectile. Practically applicable approximation schemes for computing the optical potential on different levels of sophistication can be found in the literature.[16–18] Here we only note that electron-molecule scattering calculations using optical potentials based on many-body perturbation theory have been performed with encouraging success by Klonover and Kaldor,[19] by Berman, Walter, and Cederbaum,[20] and by Berman, Mündel, and Domcke.[21] Optical potentials based on a Feshbach projection of the configurationinteraction (CI) matrix have been used by Collins and Schneider.[17,22]

The separation of the optical potential into a local and a nonlocal term strongly suggests splitting also the scattering calculation into two parts. The first step is then to solve the scattering problem for the local and long-ranged potential V. This can be very conveniently achieved by adopting a numerical progation method, i.e., by solving the coupled differential equations (or the equivalent integral equations[23]) by a finite-step method. The residual scattering due to the nonlocal interaction W can then be treated within the T-matrix expansion approach, because—due to the nonlocal and short-ranged character of the interaction—W can quite well be represented with the use of separable approximations. However, in order to perform the second step via the two potential formula one needs to know the Green's function

$$G=(E-T-V+i\eta)^{-1} \tag{1.5}$$

for the scattering by the local potential. As discussed below, the matrix elements of this Green's function can be obtained by solving a set of "driven" Schrödinger equations.

The strategy of the method outlined above is largely identical with the one of Rescigno and Orel.[12] Similar approaches are those of Schneider and Collins[11] and of Smith, Lucchese, and McKoy.[13] Our motivation was to implement a method which is most suitable for *ab initio* calculations using sophisticated many-body optical potentials. Here we discuss the method in the static exchange approximation and check our results against benchmark results in the literature.

The paper is organized as follows. In Sec. II we outline our method to compute the wave function and Green's function of the scattering by the local potential. In Sec. III we briefly describe the second step, i.e., the inclusion of the nonlocal interaction. In Sec. IV we discuss the results obtained by this method for low-energy electron scattering by H_2 and N_2 in the static exchange approximation. Section V contains a summary, a brief discussion, and suggestions for future work. Appendix A provides a brief description of the numerical algorithm used to integrate the differential equations. Appendix B describes a method to accelerate the convergence of the (local) wave function with respect to the matching radius. We have found that a simple first-order Born correction of the asymptotic wave function improves this convergence quite dramatically.

II. SCATTERING BY LOCAL NONSPHERICAL POTENTIALS

A. General theory

In order to reduce the problem to the solution of a set of ordinary differential equations we shall—as usual—expand the wave function and the Green's function into partial waves[24,25]

$$\psi(\mathbf{r})=\left[\frac{2}{\pi k}\right]^{1/2}\frac{1}{r}\sum_{l,m} i^l\psi_{lm}(r)Y_{lm}(\hat{\mathbf{r}}) , \tag{2.1}$$

$$G(\mathbf{r},\mathbf{r}')=\frac{2}{rr'}\sum_{l,l',m,m'}\hat{g}_{ll'mm'}(r,r')Y_{lm}(\hat{\mathbf{r}})Y^*_{l'm'}(\hat{\mathbf{r}}') , \tag{2.2}$$

where $\hat{\mathbf{r}}$ denotes the unit vector pointing into the direction of $\mathbf{r}$. We shall concentrate on the scattering from linear molecules. In this case m is a good quantum number and we may drop m from the equations in what follows. Next we introduce the Schrödinger operator

$$\hat{H}_{ll'}=\left[\frac{\partial^2}{\partial r^2}+k^2-\frac{l(l+1)}{r^2}\right]\delta_{ll'}-V_{ll'} , \tag{2.3}$$

where

$$V_{ll'}(r)=2\int d\hat{\mathbf{r}}Y^*_{lm}(\hat{\mathbf{r}})V(r\hat{\mathbf{r}})Y_{l'm}(\hat{\mathbf{r}}) \tag{2.4}$$

for the particular value of m under discussion. The partial wave functions ψ_l and $\hat{g}_{ll'}$ satisfy the Schrödinger equation

$$\underline{\hat{H}}\bar{\psi}=\bar{0} \tag{2.5}$$

and

$$\underline{\hat{H}}\underline{\hat{g}}(r,r')=\underline{1}\delta(r-r') \tag{2.6}$$

subject to certain boundary conditions (BC). In order to take account of these BC it is convenient to introduce the regular and irregular solution matrices defined by

$$\underline{\hat{H}}\underline{\phi}=\underline{0} , \tag{2.7a}$$

$$\phi_{ll'}(r)\underset{r\to 0}{\longrightarrow}\delta_{ll'}j_l(kr) , \tag{2.7b}$$

and

$$\underline{\hat{H}}\underline{\chi}=\underline{0} , \tag{2.8a}$$

$$\chi_{ll'}(r)\underset{r\to\infty}{\longrightarrow}\delta_{ll'}h_l^+(kr) , \tag{2.8b}$$

where j_l and h_l^+ denote the Riccati-Bessel and Hankel functions,[24] respectively. It is well known that the Green's function can be expressed by these solutions as[25]

$$\underline{\hat{g}}(r,r')=-\begin{cases}\underline{\phi}(r)\underline{W}^{-1}\underline{\chi}^T(r'), & r\leq r'\\ \underline{\chi}(r)(\underline{W}^{-1})^T\underline{\phi}^T(r'), & r>r'\end{cases} \tag{2.9}$$

where $\underline{W}$ denotes the Wronskian[25]

$$\underline{W}\equiv\underline{W}(\underline{\chi},\underline{\phi})=\underline{\chi}^T\underline{\phi}'-\underline{\chi}^{T'}\underline{\phi} . \tag{2.10}$$

The Wronskian is independent of r, since V is real and symmetric. Equation (2.9) will serve to fix the BC; it is, however, not a convenient tool to compute the Green's function.[26] For the latter purpose we shall use Eq. (2.6). Recognizing that we do not really want to know the Green's function $G(\mathbf{r},\mathbf{r}')$ but rather its matrix elements with respect to some L^2 basis functions $b_n(\mathbf{r})$, we define

$$g_{ln}(r)=\sum_{l'}\int dr'\hat{g}_{ll'}(r,r')b_{l'n}(r') , \tag{2.11}$$

where

$$b_{ln}(r)=r\int d\hat{\mathbf{r}}\,Y^*_{lm}(\hat{\mathbf{r}})b_n(r\hat{\mathbf{r}}) \tag{2.12}$$

denotes the partial-wave expansion coefficient of the nth basis function. The new functions g_{ln} satisfy [cf. Eq.

(2.6)] the driven equations

$$\sum_{l'} \hat{H}_{ll'} g_{l'n}(r) = b_{ln}(r) \ . \tag{2.13}$$

This differential equation must be solved with the correct BC. With the aid of Eq. (2.9) we find

$$g_{ln}(r) \underset{r\to 0}{\longrightarrow} \text{const}\times j_l(kr) \ , \tag{2.14}$$

$$g_{ln}(r) \underset{r\to\infty}{\longrightarrow} \text{const}\times h_l^+(kr) \ . \tag{2.15}$$

The desired matrix elements of the Green's function are finally given by

$$G_{nm} \equiv \langle n \mid G \mid m \rangle = 2\sum_{l} \int dr\, b_{ln}^*(r) g_{lm}(r) \ . \tag{2.16}$$

Rather than solving the differential equations (2.5) and (2.6) as a boundary-value problem, one may solve them with regular initial conditions at the origin and enforce the correct asymptotic BC by a linear transformation applied to the solutions. This is discussed in any textbook on scattering theory where it is shown that the properly normalized physical solution matrix is

$$\underline{\psi} = (2k/\pi)^{1/2} \underline{\phi}\, \underline{W}^{-1}(\underline{\chi},\underline{\phi}) \ . \tag{2.17}$$

[Note: The Jost matrix is $\underline{F} = k^{-1}\underline{W}(\underline{\chi},\underline{\phi})$.] Let $\tilde{g}_{ln}$ denote some regular solution of the driven equation (2.13). It is known that the general solution is the sum of $\tilde{g}_{ln}$ and any regular solution of the homogeneous equation (2.5). Hence the proper solution g_{ln} can be written as

$$g_{ln} = \tilde{g}_{ln} - \sum_{l'} \phi_{ll'} D_{l'n} \ . \tag{2.18}$$

A short calculation yields

$$\overline{\mathrm{D}}_n = \underline{W}^{-1}(\underline{\chi},\underline{\phi}) \overline{\mathrm{W}}(\underline{\chi},\overline{\mathrm{g}}_n) \ . \tag{2.19}$$

The Wronskians above have to be evaluated at an r which is large enough to ensure that all inhomogeneities have essentially vanished.

B. Numerical procedure

The numerical scheme to determine the wave function and Green's function goes as follows. At some small r_1 we set the initial conditions to be

$$\phi_{ll'}(r_1) = \delta_{ll'} j_l(kr_1) \ , \tag{2.20a}$$

$$\phi'_{ll'}(r_1) = \delta_{ll'} j'_l(kr_1) \ , \tag{2.20b}$$

$$\tilde{g}_{ln}(r_1) = 0 \ , \tag{2.21a}$$

$$\tilde{g}'_{ln}(r_1) = 0 \ . \tag{2.21b}$$

We then integrate (compare Appendix A) the set of coupled equations (2.7a) and (2.13) out to some r_2, large enough to ensure that χ takes it asymptotic form (2.8b) to a sufficient degree of accuracy. Simultaneously with the integration of the differential equation we perform the integrals

$$B_{nl} = \sum_{l'} \int_{r_1}^{r_2} dr\, b_{l'n}^*(r) \phi_{l'l}(r) \tag{2.22}$$

and

$$A_{nm} = \sum_{l} \int_{r_1}^{r_2} dr\, b_{ln}^*(r) \tilde{g}_{lm}(r) \tag{2.23}$$

using Simpson's rule. At the end of the calculation we transform to the correct BC, yielding

$$G_{nm} = 2A_{nm} - 2\sum_{l'} B_{nl'} D_{l'm} \ , \tag{2.24}$$

$$\Psi_{nl} = (2k/\pi)^{1/2} \sum_{l'} B_{nl'} [W^{-1}(\underline{\chi},\underline{\phi})]_{l'l} \ , \tag{2.25}$$

$$\underline{K}^{(\mathrm{L})} = \underline{W}(\mathrm{Im}\underline{\chi},\underline{\phi}) \underline{W}^{-1}(-\mathrm{Re}\underline{\chi},\underline{\phi}) \ . \tag{2.26}$$

Here $\underline{K}^{(\mathrm{L})}$ denotes the K matrix for the scattering by the local potential. The superscript L refers to local. The symbol Ψ_{nl} denotes the overlap of the nth basis function with that component of the physical wave function which is a pure l state initially. All three matrices defined above are needed for the second step, i.e., the inclusion of the nonlocal interaction.

Before we conclude this section we have to mention two technical modifications which we have ignored so far. Firstly, it is well known[27] that the solution matrices have to be stabilized because their column vectors tend to become linearly dependent due to the exponential growth in the closed channels. Our stabilization procedure, which is similar to the one used by Rescigno and Orel,[28] is described in Appendix A. The second remark concerns the irregular (or Jost) solution χ. One usually integrates the regular solutions to such a large r_2 that the Riccati-Hankel functions $h^+(kr)$ become a sufficiently good approximation to χ. The final matching equations (2.24)–(2.26), however, can be performed at a considerably smaller r_2 if one computes an approximation to χ by perturbation theory. This *very* helpful simple modification is discussed in Appendix B. Finally we remark that both the Green's and the K matrix are symmetric. Furthermore, the unitarity of the S matrix requires that

$$\pi \sum_{l} \Psi_{nl}^* \Psi_{ml} = -\mathrm{Im}(G_{nm}) \tag{2.27}$$

holds. These three requirements serve as a useful check on the accuracy of the numerical calculation.

III. SCATTERING BY THE NONLOCAL POTENTIAL

The scattering by the nonlocal potential W will be treated within the framework of the T-matrix expansion method.[5,6] We approximate the interaction W by the truncated separable form

$$W \rightarrow \sum_{n,m=1}^{N} \mid b_n \rangle W_{nm} \langle b_m \mid \tag{3.1}$$

where

$$W_{nm} = \langle b_n \mid W \mid b_m \rangle \tag{3.2}$$

and find that the on-shell T matrix is given by[6]

$$T_{ll'}^{(\mathrm{NL})} = \sum_{n,n',n''=1}^{N} \Psi_{nl}^* (\underline{1} - \underline{W}\,\underline{G})_{nn'}^{-1} W_{n'n''} \Psi_{n''l'} \tag{3.3}$$

(the superscript NL referres to "nonlocal"). This equation can be written more symmetrically as

$$\underline{T}^{(\mathrm{NL})}=\underline{\Psi}^{\dagger}\underline{W}(\underline{W}-\underline{W}\,\underline{G}\,\underline{W})^{-1}\underline{W}\,\underline{\Psi}\ , \tag{3.4}$$

which has a form similar to the Schwinger variational expression for the T matrix.[7] However, Eq. (3.4), as it stands, is not a variational expression. The variational stability is only achieved if the operator products $W\Psi$ and WGW are done exactly, i.e., either numerically or with a *complete* basis. Equation (3.4), however, suggests the introduction of two basis sets. The smaller basis—called the inversion basis—is the one in which the operator W-WGW is inverted. The larger basis—called quadrature basis[21,29]—is used to perform the matrix products $W\Psi$ and WGW. The inversion basis is usually a subset of the quadrature basis. If both basis sets are equal, Eq. (3.4) becomes identical with Eq. (3.3).

Two technical remarks are necessary. First, Eq. (3.1), (3.3), and (3.4) are valid only for an orthonormal basis. For non-orthonormal basis sets Eq. (3.4) should read

$$\underline{T}^{(\mathrm{NL})}=\underline{\Psi}^{\dagger}\underline{S}^{-1}\underline{W}(\underline{W}-\underline{W}\,\underline{S}^{-1}\underline{G}\,\underline{S}^{-1}\underline{W})^{-1}\underline{W}\,\underline{S}^{-1}\underline{\Psi}\ , \tag{3.5}$$

where

$$S_{nm}=\langle b_n \mid b_m \rangle \tag{3.6}$$

denotes the overlap matrix. Second, a large basis set consisting of, say, Cartesian Gaussians has the tendency to become linearly dependent. An almost linear dependence manifests itself in a small eigenvalue of S and hence in huge matrix elements of S^{-1}. This leads to numerical instabilities. A solution to this problem is to replace S^{-1} by $\hat{S}$ in Eq. (3.5) where

$$\hat{\underline{S}}=(\underline{1}-\underline{P})\underline{S}^{-1}(\underline{1}-\underline{P})\ , \tag{3.7}$$

and where P denotes the projector on the one (or the few) linear combinations of basis functions for which the eigenvalue of S is almost vanishing. In practice, $\hat{S}$ is evaluated by first diagonalizing S. We take the reciprocal of all eigenvalues of S except those which are smaller than some threshold ϵ. The latter are set to zero. The matrix $\hat{S}$ is finally obtained by transforming back with the aid of the eigenvector matrix. The final step of the calculation is to obtain the total S matrix (not to be confused with the overlap matrix). The S matrices for the scattering by the local and nonlocal potential are given by

$$\underline{S}^{(L)}=(\underline{1}+i\underline{K}^{(L)})(\underline{1}-i\underline{K}^{(L)})^{-1}\ , \tag{3.8}$$

$$\underline{S}^{(\mathrm{NL})}=\underline{1}-2\pi i T^{(\mathrm{NL})}\ , \tag{3.9}$$

and the total S matrix is just the product

$$\underline{S}=\underline{S}^{(L)}\underline{S}^{(\mathrm{NL})} \tag{3.10}$$

of the two S matrices. The total K matrix is finally given by

$$\underline{K}=-i(\underline{S}-\underline{1})(\underline{S}+\underline{1})^{-1}\ . \tag{3.11}$$

This completes the electron-molecule scattering calculation in the fixed-nuclei limit.

IV. RESULTS

In order to demonstrate the feasibility and accuracy of the present method we have performed scattering calculations for $e^- + H_2$ and $e^- + N_2$ on the static exchange level. The first step is to perform an SCF calculation for the target molecule. We have used the same SCF basis sets as Watson *et al.*[29] for H_2 and as Berman and Domcke[30] for N_2. The second step is to expand the local (i.e., static) potential

$$V(\mathbf{r})=\sum_{\lambda=0}^{\lambda_{\max}} V_{\lambda}(r)Y_{\lambda 0}(\hat{\mathbf{r}}) \tag{4.1}$$

and evaluate $V_{\lambda}(r)$ at a certain number of grid points. We have used $\lambda_{\max}=40$ (H_2) or $\lambda_{\max}=98$ (N_2) and 600 (H_2) or 1000 (N_2) grid points, respectively. For large r we used the multipole expansion of the static potential. The third step is to compute the matrix elements of the nonlocal (i.e., exchange) potential W. The quadrature basis, i.e., the basis in which W is expanded, can be chosen quite independently of the SCF basis. The fourth step is to in-

TABLE I. Basis set for the e^--H_2 scattering calculation. We have used Cartesian Gaussians. The type z is a short-hand notation for a p_z function, etc. The functions are located either at the atoms or at the center of the molecule. In the case of the Σ_g symmetry we used all 27 functions as quadrature basis but removed the three lowest eigenvalues from the overlap matrix [cf. Eq. (3.7)]. The basis functions used to form the inversion basis are indicated by an asterisk (*). In the case of the Σ_u symmetry we simply took the first 13 functions to form both the quadrature and the inversion basis.

Number	Location	Type	Exponent
1	0.7003	*s*	9.0*
2	0.7003	*s*	5.0
3	0.7003	*s*	3.0*
4	0.7003	*s*	1.7*
5	0.7003	*s*	1.0
6	0.7003	*s*	0.6*
7	0.7003	*s*	0.35*
8	0.7003	*s*	0.2*
9	0.7003	*z*	3.5*
10	0.7003	*z*	2.0*
11	0.7003	*z*	1.2*
12	0.7003	*z*	0.7*
13	0.7003	*z*	0.4*
14	0.0	*s*	2.0
15	0.0	*s*	1.0
16	0.0	*s*	0.5
17	0.0	*s*	0.25
18	0.0	*s*	0.15
19	0.0	*s*	0.09*
20	0.0	*s*	0.05
21	0.0	*zz*	2.0
22	0.0	*zz*	1.0
23	0.0	*zz*	0.5
24	0.0	*zz*	0.25*
25	0.0	*zz*	0.15*
26	0.0	*zz*	0.09*
27	0.0	*zz*	0.05

TABLE II. K-matrix elements of the e^--H_2 scattering system in Σ symmetries. CRM: Ref. 31, the K-matrix elements, however, are published in Ref. 29. WLM: Ref. 29. LWM: Ref. 32. Numbers in square brackets represent multiplication by powers of ten, e.g., $1[2]=1\times10^2$.

	K_{00}				K_{02}				K_{22}			
k	CRM	WLM	LWM	Present	CRM	WLM	LWM	Present	CRM	WLM	LWM	Present
1.0	8.05	8.07	8.04	8.044	0.11	0.039	0.122	0.1213	0.093	0.092	0.0914	0.091 56
0.8				−8.580				−0.0303				0.054 78
0.7	−3.88	−3.85		−3.839	0.0093	0.025		0.0043	0.039	0.036		0.036 54
0.6	−2.32	−2.32		−2.318	0.015	0.016		0.0120	0.027	0.025		0.024 82
0.5	−1.55	−1.55	−1.55	−1.548	0.015	0.0094	0.0134	0.0133	0.018	0.017	0.0163	0.016 44
0.4	−1.07	−1.06		−1.066	0.013	0.0048		0.0122	0.011	0.014		0.010 83
0.3	−0.722	−0.718	−0.722	−0.7217	0.011	0.0002	0.009 78	0.0098	0.0074	0.0086	0.0069	0.007 10
0.2	−0.451	−0.444		−0.4499	0.0073	0.0006		0.0067	0.0045	0.0025		0.004 40
0.1	−0.217	−0.211	−0.217	−0.2164	0.0039	0.76[−4]	0.004 06	0.0034	0.0021	0.0013	0.0017	0.002 16

	K_{11}				K_{13}				K_{33}			
k	CRM	WLM	LWM	Present	CRM	WLM	LWM	Present	CRB	WLM	LWM	Present
1.0	1.34	1.332	1.34	1.343	0.029	0.033	0.0304	0.0302	0.0202	0.015	0.0190	0.01880
0.8				1.066				0.0192				0.01094
0.7	0.863	0.854		0.8589	0.014	0.016		0.0141	0.0093	0.0095		0.00846
0.6	0.638	0.627		0.6293	0.010	0.011		0.009 89	0.0072	0.0080		0.00663
0.5	0.421	0.409	0.411	0.4109	0.0071	0.0079	0.00703	0.006 76	0.0056	0.0064	0.0052	0.00523
0.4	0.243	0.233		0.2341	0.0049	0.0053		0.004 61	0.0043	0.0053		0.00408
0.3	0.119	0.112	0.113	0.1130	0.0034	0.0039	0.00335	0.003 13	0.0031	0.0036	0.0029	0.00303
0.2	0.0463	0.0428		0.0439	0.0023	0.0027		0.002 00	0.0020	0.0022		0.00202
0.1	0.0127	0.0108	0.123	0.0124	0.0015	0.0008	0.00105	0.000 99	0.73[−3]	0.11[−3]	0.971[−3]	0.00101

TABLE III. Eigenphase sums of the e^--H_2 scattering system in Σ symmetries. CRM: Ref. 31. NBS: Ref. 33.

	$\delta(\Sigma_g)$			$\delta(\Sigma_u)$		
k	NBS	CRM	Present	NBS	CRM	Present
1.0	1.4352	1.5509	1.5527	0.9310	0.9591	0.9603
0.8	1.7277	1.7509	1.7504	0.8086	0.8361	0.8371
0.7	1.8583	1.8729	1.8725	0.7239	0.7269	0.7257
0.6	2.0024	2.0114	2.0116	0.5694	0.5797	0.5748
0.5	2.1612	2.1679	2.1680	0.4032	0.4084	0.4005
0.4	2.3356	2.3399	2.3407	0.2421	0.2459	0.2383
0.3	2.5229	2.4276	2.5278	0.1204	0.1233	0.1187
0.2	2.7229	2.7246	2.7260	0.0481	0.0493	0.0480
0.1	2.9302	2.9303	2.9319	0.0128	0.0134	0.0144

tegrate the wave function and the Green's function of the local problem for all desired energies. Finally the fifth step—called the T-matrix calculation in the following—is to evaluate Eq. (3.5) and to compute the total K matrix.

It was found that the integration of the wave function and Green's function of the local scattering problem shows a stable and uniform convergence with respect to both the number of coupled channels included and the choice of the matching radius r_2. The convergence of the T-matrix calculation with respect to the size of the basis set, however, was found to be slow and nonuniform. A quite small basis set is capable of accounting for the major effects of the exchange scattering, e.g., with only four functions one can reproduce the K_{00} matrix elements and the eigenphase sums of the e^--H_2 ${}^2\Sigma_g^+$ scattering to within 10%. To obtain very accurate data, however, one needs a very large basis set and is then plagued with numerical instabilities while solving Eq. (3.5). Taking the quadrature basis and the inversion basis to be different one finds that the convergence with respect to the inversion basis is well behaved. The slow and erratic performance of the convergence is apparently due to the quadrature basis. Hence the instability of the T-matrix calculation is expected to disappear if one avoids the introduction of a quadrature basis (see Sec. V).

For e^--H_2 scattering on the static exchange level there are very accurate data available. To compare with these benchmark data we have chosen to use a fairly large quadrature basis. This basis set is given in Table I. In Tables II and III we compare the K-matrix elements and eigenphase sums of the present calculation with those of Collins, Robb, and Morrison (CRM) (Ref. 31), of Watson, Lucchese, and McKoy (WLM) (Ref. 29) and (LWM) (Ref. 32), and of Noble, Burke, and Salvini (NBS) (Ref. 33). The target SCF orbital of the present calculation is the same as the one used by WLM and LWM whereas CRM and NBS have used the Slater-type orbital given by Fraga and Ransil.[34] The iterative close-coupling calculation of CRM and the iterative Schwinger calculation of LWM are regarded as the most accurate data available for the e^--H_2 scattering system. The agreement of the presently calculated K-matrix elements and eigenphase sums with these data is excellent. It is interesting to note that the different representations of the target apparently influence the scattering only marginally.

We now turn to the e^--N_2 scattering system. Table IV gives the quadrature basis set. In Table V we compare our eigenphase sums with those obtained by CRM (Ref. 31), by NBS (R-matrix calculation) (Ref. 33), by Weatherford, Onda, and Temkin (WOT) (noniterative partial differential equation method) (Ref. 35), and by Collins and

TABLE IV. Basis set for the e^--N_2 calculation in the Σ symmetries. See caption of Table I for details. We have used the same basis set for both the Σ_g and the Σ_u symmetry, except for taking the last six functions of s type for the Σ_g and of p_z type for the Σ_u symmetry. The quadrature basis consists of all the 22 functions shown. In Σ_u symmetry, however, the two lowest eigenvalues of the overlap matrix are removed [cf. Eq. (3.7)]. The 17 functions indicated by an asterisk (*) form the inversion basis. The basis set for the Π symmetries is quite similar to the one for the Σ symmetries except for (i) deleting the first function and (ii) replacing all s- and z-type functions by x- and xz-type functions, respectively. For both Π symmetries we took all 21 functions to form both the quadrature and the inversion basis.

Number	Location	Type	Exponent
1	1.034 65	s	20.0*
2	1.034 65	s	9.0*
3	1.034 65	s	5.0*
4	1.034 65	s	3.0*
5	1.034 65	s	1.7*
6	1.034 65	s	1.0*
7	1.034 65	s	0.6
8	1.034 65	s	0.35*
9	1.034 65	s	0.2*
10	1.034 65	s	0.12*
11	1.034 65	z	3.5*
12	1.034 65	z	2.0*
13	1.034 65	z	1.2*
14	1.034 65	z	0.7*
15	1.034 65	z	0.4*
16	1.034 65	z	0.25*
17	0.0	s,z	2.0
18	0.0	s,z	1.0*
19	0.0	s,z	0.5
20	0.0	s,z	0.25
21	0.0	s,z	0.15*
22	0.0	s,z	0.09

Schneider (CS) (linear algebraic approach). All investigators have used the target wave function of Cade, Sales, and Wahl[36] except for NBS, who have used Nesbet's target[37] and the present calculation where the SCF basis of Ref. 30 has been used. The eigenphase sums obtained by the present approach again agree excellently with the literature data. In Table VI we furthermore compare the total cross sections of the present calculation with those obtained by CRM and WOT. The e^--N_2 eigenphase sums of the present calculation are also shown in Figs. 1 and 2. There the eigenphase sums are divided into their static and their exchange contributions. One notices that the exchange contribution is not small. The Π_g eigenphase sum is of particular interest. There the static potential is almost completely shielded by the centrifugal barrier. It needs the attractive exchange interaction to surmount the barrier and to create the well-known shape resonance. Figure 3 shows the total cross sections of the four symmetries discussed above and the contribution of the Δ_g symmetry. The solid line in Fig. 3 represents the

TABLE V. Eigenphase sums (modulo π) of the e^--N_2 scattering system. CRM: Ref. 31. NBS: Ref. 33. WOT: Ref. 35. CS: Results of Collins and Schneider published in Ref. 35.

		e^--$N_2\,^2\Sigma_g^+$ eigenphase sum			
E (Ry)	CRM	NBS	WOT	CS	Present
1.00	1.043	1.229	1.350	1.296	1.295
0.75	1.263	1.504			1.496
0.50	1.524	1.771	1.747	1.723	1.726
0.40	1.654	1.872			1.838
0.30	1.808	2.003	1.983		1.976
0.20	2.011	2.182			2.158
0.10	2.311	2.433	2.417	2.406	2.425
0.05	2.544	2.634			2.630
0.01	2.874	2.924			2.913
0.001	3.057				3.057
		e-$N_2\,^2\Sigma_u^+$ eigenphase sum			
1.00	1.908	2.031	2.149		2.081
0.75	2.073	2.221			2.187
0.50	2.316	2.457	2.479		2.400
0.40	2.440	2.564			2.512
0.30	2.584	2.702	2.692		2.636
0.20	2.749	2.844			2.773
0.10	2.937	2.988	2.976		2.933
0.05	3.038	3.072			3.028
0.01	3.119	3.124			3.111
0.001					3.134
		e^--$N_2\Pi_u$ eigenphase sum			
1.00	−0.694	−0.773	−0.646		−0.681
0.75	−0.601	−0.578			−0.590
0.50	−0.455	−0.423	−0.536		−0.443
0.40	−0.379	−0.369			−0.367
0.30	−0.290	−0.264	−0.269		−0.279
0.20	−0.189	−0.155			−0.177
0.10	−0.075	−0.065	−0.0705		−0.069
0.05					−0.020
0.01					+0.003
		e^--$N_2\Pi_g$ eigenphase sum			
1.00	2.453	2.456	2.546		2.462
0.75	2.484	2.487			2.498
0.50	2.454	2.546	2.574		2.442
0.40	2.316	2.442			2.370
0.30	1.461	1.831	1.760		1.639
0.20	0.202	0.245			0.215
0.10	0.011	0.026	0.0105		0.011
0.05					0.008
0.01					−0.005

TABLE VI. Cross sections σ_{tot} (in atomic units) for the e^--N_2 scattering system. CRM: Ref. 31. WOT: Ref. 35.

E (Ry)	CRM	WOT	Present	CRM	WOT	Present
		Σ_g			Σ_u	
1.00	11.04	12.51	12.42	11.90	10.36	10.55
0.75	15.87		16.78	13.24		10.87
0.50	25.13	24.30	24.33	13.42	9.89	10.14
0.40	31.12		29.98	12.71		9.44
0.40		34.84	35.12	11.23	7.64	8.52
0.20	50.60		43.10	8.69		7.16
0.10	66.67	53.39	52.56	4.81	3.08	4.68
0.05	77.20		57.19	2.48		2.70
0.01	84.35		60.27	0.76		0.91
		Π_g			Π_u	
1.00	9.94	8.45	9.47	12.05	11.24	11.56
0.75	12.14		11.36	11.34		10.85
0.50	19.69	14.55	17.90	10.43	8.75	8.92
0.40	33.29		29.44	8.00		7.55
0.30	82.99	80.65	83.38		5.69	5.68
0.20	55.77		6.45	3.82		3.27
0.10	0.93	0.45	0.12	1.20	1.04	0.84

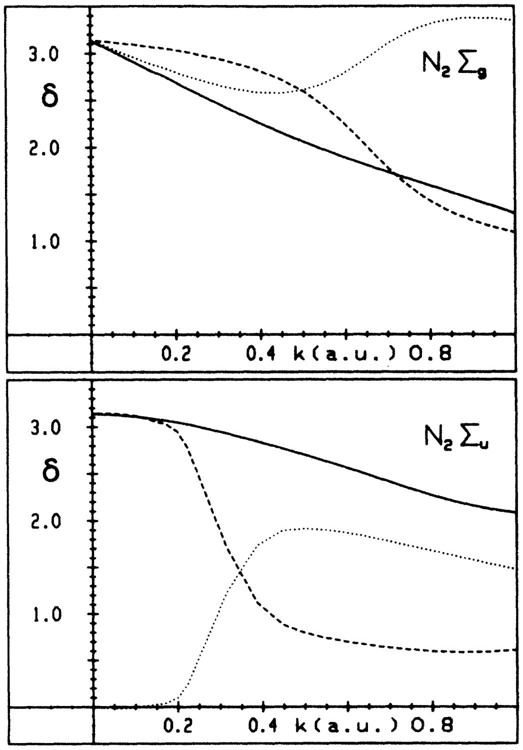

FIG. 1. Eigenphase sums of the e^--N_2 scattering system vs initial momentum k. The solid line represents the (total) eigenphase sum [i.e., $\delta=(2i)^{-1}\ln(\det S)$], the dashed line represents the exchange eigenphase sum [i.e., $\delta_{ex}=(2i)^{-1}\ln(\det S^{(NL)})$], and the dotted line represents the static eigenphase sum [i.e., $\delta_{st}=(2i)^{-1}\ln(\det S^{(L)})$]. Shown are $\delta-2\pi$, δ_{ex}, and $\delta_{st}-\pi$ in Σ_g and $\delta-\pi$, δ_{ex}, and $\delta_{st}-\pi$ in Σ_u symmetry.

sum of the five contributions.

It is interesting to note that the instability problem of the T-matrix approach—discussed at length above—heavily depends on the symmetry of the scattering process. In the case of the e^--H_2 systems the instability problem disappears if we go from the Σ_g to the Σ_u symmetry. The Σ_u results remain essentially unchanged when we take into account only the first eight functions rather than the first 13 functions of the basis given in Table I. A similar trend was found in the calculations for N_2. The stability of the T-matrix calculation significantly increases when one goes from the Σ_g to Σ_u, Π_u and Π_g symmetry. To illuminate this effect we mention that we estimate the error in the exchange eigenphase sums to be smaller than 0.06, 0.03, 0.02, and 0.015 rad for the Σ_g, Σ_u, Π_u, and Π_g symmetries, respectively. The error in the static eigenphase sums, on the other hand, is estimated to be smaller than $(3\times10^{-3})(0.1+k)$ rad for all symmetries. (k denotes the initial momentum in a.u.) The increase in the stability of the T-matrix calculation is apparently related to the buildup of the centrifugal barrier which lessens the influence of the short-ranged exchange. In particular the wave functions in the Π symmetries show a nodal line along the internuclear axis. Hence the Π wave functions vanish where the exchange interaction is strong, namely at the nuclei.

As a final remark we mention that the computation of the wave function and Green's function for the static N_2 potential takes between 1 and 3 minutes CPU time on an IBM 3081D. Computations performed at higher energies require more angular momenta and hence consume more computation time than those performed at lower energies. The evaluation of Eq. (3.5), i.e., the T-matrix calculation, takes only a few seconds.

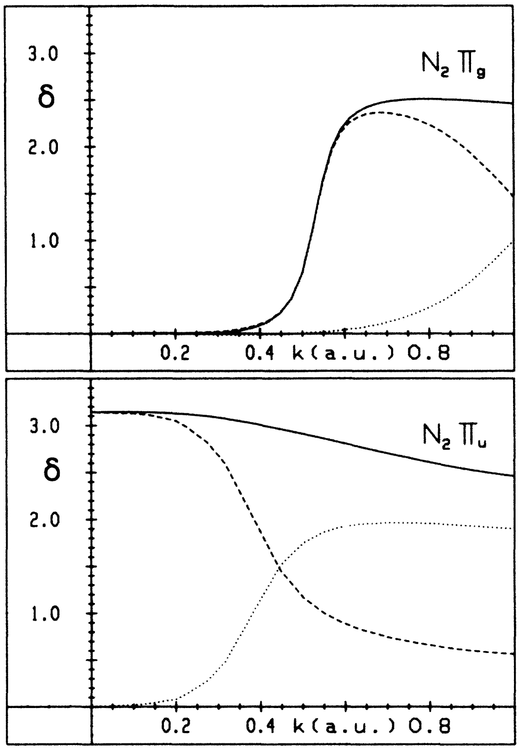

FIG. 2. Similar to Fig. 1, however, no multiples of π are substracted from the eigenphase sums.

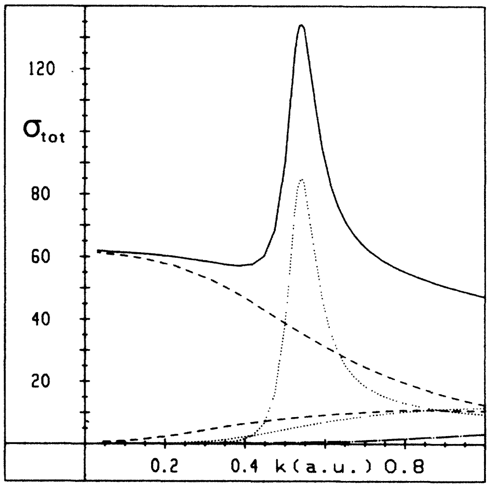

FIG. 3. Total cross section (in atomic units) vs the initial momentum. The contribution of the Σ symmetries are shown as dashed lines and those of the Π symmetries as dotted lines. The contribution of the Δ_g symmetry is shown as a dashed-dotted line. The contribution of the Δ_u symmetry was found to be negligible. The solid line represents the sum of the five contributions.

V. DISCUSSION

The method which we have described above is similar to the one of Rescigno and Orel.[12] There are two major differences. Firstly, Rescigno and Orel solve Volterra-type integral equations[23] whereas we solve differential equations to obtain the wave function for the local scattering problem (see Appendix A). Similarly to the above calculations they also use Cartesian Gaussians as inhomogeneities of the Schrödinger equation. However, they transform to the correct BC and thereby extract the (full) K matrix in one step whereas we first transform to the BC of the local problem and then solve for the nonlocal scattering by another matrix inversion. The advantage of the explicit construction of (the matrix elements of) the Green's function lies in the direct applicability of the Feshbach projection formalism for shape resonances.[21,30,38] This formalism allows for the computation of the resonance width Γ and the level shift Δ of some predetermined discrete state. The quantities Γ and Δ are important input data for calculating the vibrational excitation of a molecule by electron impact in the neighborhood of a shape resonance[38-41] as well as for the treatment of dissociative attachment.[41] To implement the Feshbach formalism for shape resonances one merely has to replace the free Green's function by the one of the local scattering problem and the full potential by its nonlocal part and all the derivations of Refs. 21 and 30 remain valid. This in particular distinguishes the present approach from all those approaches which—like the R-matrix method—do not construct a Green's function.

More generally we would like to mention that the explicit separation of the scattering problem into two subproblems is also of advantage computationally. The convergence properties of both subproblems can be studied independently. In particular, because the T-matrix calculation is very fast, one can extensively investigate its convergence using different subsets of the basis in which the Green's function is expanded.

The scattering off the local potential is treated by a close-coupling method. This method has been used in electron-molecule scattering before, e.g., by Burke and coworkers.[42] The single center expansion, which is used in the close-coupling formalism, has sometimes been criticized in the literature. Our experience is that the convergence with respect to the angular momenta is very well behaved (albeit not very fast). Moreover, the angular momentum representation very conveniently allows us to evaluate the wave function for large l and for large r by the Born approximation. The former modification[43] has not been implemented yet, the latter one, which is described in detail in Appendix B, was found to be very helpful. It will be of great importance if the molecule possesses a dipole moment.

A possible extension of the present method is the implementation of a full Schwinger variational calculation. The introduction of a quadrature basis can be avoided by using

$$\hat{b}_n = W b_n \tag{5.1}$$

as inhomogeneities [cf. Eqs. (2.12) and (2.16)]. Doing so one computes $\langle \Psi_l \,|\, W \,|\, n \rangle$ and $\langle n \,|\, WGW \,|\, m \rangle$ rather than $\langle \Psi_l \,|\, n \rangle$ and $\langle n \,|\, G \,|\, m \rangle$. Hence one can now perform an *exact* Schwinger variational calculation. The additional work of evaluating Eq. (5.1) and expanding $\hat{b}_n$ on an $r \times l$ grid will be compensated by the smaller number of basis functions which are now necessary. However, when going beyond the static exchange level, W becomes energy dependent and Eq. (5.1) has to be evaluated for each energy point. It then becomes questionable if there is still a computational advantage. In any case, using the $\hat{b}_n$ as inhomogeneities one follows a similar route as recently taken by Smith, Lucchese, and McKoy.[13]

In concluding this article we want to emphasize again that the two major advantages of the present approach to the fixed-nuclei electron-molecule scattering lie in the straightforward way to, firstly, use a full many-body optical potential rather than the static exchange one and, secondly, to perform a Feshbach projection for shape resonances. Work along these lines is in progress.

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APPENDIX A

We want to numerically solve the differential equation

$$\bar{y}'' + \underline{G}\bar{y} = \bar{b} , \tag{A1}$$

where $\bar{y}$ denotes some column vector of the matrices $\underline{\phi}$ or $\underline{g}$, $\bar{b}$ denotes the coefficient vector of an inhomogeneity, and $\underline{G}$ is defined by

$$G_{ll'}(r) = \delta_{ll'}[k^2 - l(l+1)/r^2] - V_{ll'}(r) . \tag{A2}$$

We introduce the finite step size h, define the abbreviations

$$\begin{aligned} \bar{y}_- &= \bar{y}(r-h) , \\ \bar{y}_0 &= \bar{y}(r) , \\ \bar{y}_+ &= \bar{y}(r+h) , \end{aligned} \tag{A3}$$

and assume similar equations for $\underline{G}$ and $\bar{b}$. The propagation of the solution is then performed by the equations

$$\bar{y}_+^{(1)} = 2\bar{y}_0 - \bar{y}_- + h^2 \underline{G}_0 \bar{y}_0 + h^2(\bar{b}_+ + 10\bar{b}_0 + \bar{b}_-)/12 , \tag{A4}$$

$$\bar{y}_+^{(2)} = \bar{y}_+^{(1)} - h^2(\underline{G}_+ \bar{y}_+^{(1)} - 2\underline{G}_0 \bar{y}_0 + \underline{G}_- \bar{y}_-)/12 , \tag{A5}$$

$$\bar{y}_+ = \bar{y}_+^{(2)} - h^2 \underline{G}_+ (\bar{y}_+^{(2)} - \bar{y}_+^{(1)})/30 . \tag{A6}$$

Equations (A4) and (A5) are known as the Störmer algorithm,[44] the modification (A6) is due to Baylis.[45] Each integration step requires two matrix multiplications, namely, $\underline{G}_+ \bar{y}_+^{(1)}$ and $\underline{G}_+ \bar{y}_+^{(2)}$. $\underline{G}_+ \bar{y}_+$ is not evaluated. In the following integration step we use the already evaluated quantity $\underline{G}_0 \bar{y}_0^{(2)}$ rather than $\underline{G}_0 \bar{y}_0$. In order to be able to double the step size we keep three solution matrices (the column vectors of which are the $\bar{y}$'s) and three derivative matrices (the column vectors of which are $\underline{G}\bar{y}$) in core. The error in the integration is of the order h^6. The derivative $\bar{y}_0'$ which is needed to evaluate the Wronskians at the end of the integration is obtained by the formula

$$\bar{y}_0' = \frac{1}{2h} \left[\bar{y}_+ - \bar{y}_- + \frac{h^2}{6} (\underline{G}_+ \bar{y}_+ - \underline{G}_- \bar{y}_- - \bar{b}_+ + \bar{b}_-) \right] + O(h^5) . \tag{A7}$$

To minimize roundoff errors, the solutions have to be stabilized.[27,28] Assume we want to stabilize the solutions at some predetermined set of points $\{r_j\}$. The regular solution within the interval $[r_j, r_{j+1}]$ is called $\underline{\phi}^{(j)}$ and similar for the other quantities. We replace equations (2.22) and (2.23) by

$$\tilde{A}_{nm}^{(j)} = A_{nm}^{(j-1)} + \sum_l \int_{r_{j-1}}^{r_j} dr\, b_{ln}^*(r) \tilde{g}_{ln}^{(j-1)}(r) , \tag{A8}$$

$$\tilde{B}_{nl}^{(j)} = B_{nl}^{(j-1)} + \sum_{l'} \int_{r_{j-1}}^{r_j} dr\, b_{l'n}^*(r) \phi_{l'l}^{(j-1)}(r) , \tag{A9}$$

where the integrals are performed by Simpson's rule and define

$$\underline{T} = [\underline{\phi}^{(j-1)}(r_j)]^{-1} , \tag{A10}$$

$$\underline{f} = \underline{\tilde{g}}^{(j-1)}(r_j) . \tag{A11}$$

At $r = r_j$ the stabilization performs as follows:

$$\underline{\phi}_0^{(j)} = \underline{\phi}_0^{(j-1)} \underline{T} , \tag{A12}$$

$$\underline{\phi}_-^{(j)} = \underline{\phi}_-^{(j-1)} \underline{T} , \tag{A13}$$

$$\underline{\tilde{g}}_0^{(j)} = \underline{\tilde{g}}_0^{(j-1)} - \underline{\phi}_0^{(j)} \underline{f} , \tag{A14}$$

$$\underline{\tilde{g}}_-^{(j)} = \underline{\tilde{g}}_-^{(j-1)} - \underline{\phi}_-^{(j)} \underline{f} , \tag{A15}$$

$$\underline{B}^{(j)} = \underline{\tilde{B}}^{(j)} \underline{T} , \tag{A16}$$

$$\underline{A}^{(j)} = \underline{\tilde{A}}^{(j)} - \underline{B}^{(j)} \underline{f} . \tag{A17}$$

APPENDIX B

This appendix is concerned with a perturbative evaluation of the Jost solution $\mathcal{X}$. The procedure described below allows us to stop the integration of the coupled equations at a considerably smaller value of the matching radius r as compared to the usual procedure of identifying the Jost solution with the free solution h^+.

We shall write the Jost solution $\mathcal{X}(r)$ as

$$\underline{\mathcal{X}}(r) = \underline{h}^+(kr) \underline{A}(r) + \underline{h}^-(kr) \underline{B}(r) \tag{B1}$$

and

$$\underline{\mathcal{X}}'(r) = k \underline{h}^{+\prime}(kr) \underline{A}(r) + k \underline{h}^{-\prime}(kr) \underline{B}(r) . \tag{B2}$$

The matrices $\underline{A}$ and $\underline{B}$ are given by the integral equations[24]

$$\underline{A}(r)=\underline{1}-(2ik)^{-1}\int_r^\infty dr'\underline{h}^{-}\underline{V}(\underline{h}^{+}\underline{A}+\underline{h}^{-}\underline{B})\,, \tag{B3}$$

$$\underline{B}(r)=(2ik)^{-1}\int_r^\infty dr'\underline{h}^{+}\underline{V}(\underline{h}^{+}\underline{A}+\underline{h}^{-}\underline{B})\,. \tag{B4}$$

Replacing V by λV and writing A and B as

$$\underline{A}=\underline{1}+\lambda\underline{A}^{(1)}+\lambda^2\underline{A}^{(2)}+\cdots\,, \tag{B5}$$

$$\underline{B}=\lambda B^{(1)}+\lambda^2\underline{B}^{(2)}+\cdots\,, \tag{B6}$$

one finds that the first-order corrections are given by

$$\underline{A}^{(1)}=-(2ik)^{-1}\int_r^\infty dr'\underline{h}^{-}\underline{V}\underline{h}^{+}\,, \tag{B7}$$

$$\underline{B}^{(1)}=(2ik)^{-1}\int_r^\infty dr'\underline{h}^{+}\underline{V}\underline{h}^{+}\,. \tag{B8}$$

We expand $V_{ll'}(r)$ in inverse powers

$$V_{ll'}(r)=\sum_n V_{nll'}r^{-n} \tag{B9}$$

and recognize that the Riccati-Hankel functions can be written as

$$h_l^{\pm}(kr)=Q_l(\pm kr)\exp[\pm i(kr-l\pi/2)]\,, \tag{B10}$$

where

$$Q_l(x)=\sum_{j=0}^{l}\frac{(l+j)!}{j!(l-j)!}(-2ix)^{-j}$$

$$=\sum_{j=0}^{l}q_j^{(l)}(-2ix)^{-j}\,. \tag{B11}$$

After a short calculation one finds that the first-order corrections (B7) and (B8) can be written as

$$A_{ll'}^{(1)}=-(2ik)^{-1}i^{l-l'}\sum_n\sum_{j=0}^{l}\sum_{j'=0}^{l'}V_{nll'}q_j^{(l)}q_{j'}^{(l')}(2ikr)^{-j}(-2ikr)^{-j}(j+j'+n-1)^{-1}r^{-n+1}\,, \tag{B12}$$

and

$$B_{ll'}^{(1)}=-(2ik)^{-2}(-i)^{l+l'}e^{2ikr}\sum_n\sum_{j=0}^{l}\sum_{j'=0}^{l'}V_{nll'}q_j^{(l)}q_{j'}^{(l')}(-2ikr)^{-j-j'}r^{-n}f(j+j'+n,kr)\,, \tag{B13}$$

where

$$f(N,kr)=\int_0^\infty dx\,e^{-x}(1-x/2ikr)^{-N}\,. \tag{B14}$$

The last integral can be evaluated very efficiently by Gauss-Laguerre integration.[46]

One may follow the route outlined above to obtain the second-order correction. However, the evaluation of the second-order corrections becomes very time consuming because there are now four nested sums going from zero to l or l'. A very efficient way to improve the results is to require that the Wronski relation and the symmetry of the S matrix are obeyed to second order. The Wronskian $W(\mathcal{X}^*,\mathcal{X})$ is easily evaluated,

$$\underline{W}(\underline{\mathcal{X}}^*,\underline{\mathcal{X}})=2ik(\underline{A}^\dagger\underline{A}-\underline{B}^\dagger\underline{B})\,. \tag{B15}$$

Because the Wronskian is independent of r, the exact solution satisfies

$$\underline{A}^\dagger\underline{A}=\underline{1}+\underline{B}^\dagger\underline{B}\,, \tag{B16}$$

or, to second order,

$$\underline{A}^{(2)}+(\underline{A}^{(2)})^\dagger=(\underline{B}^{(1)})^\dagger\underline{B}^{(1)}-(\underline{A}^{(1)})^\dagger\underline{A}^{(1)}\,. \tag{B17}$$

Hence the Hermitian part $\underline{A}_H^{(2)}$, of the second-order correction of $\underline{A}$ is very easy to obtain,

$$\underline{A}_H^{(2)}=\tfrac{1}{2}[(\underline{B}^{(1)})^\dagger\underline{B}^{(1)}-(\underline{A}^{(1)})^\dagger\underline{A}^{(1)}]\,. \tag{B18}$$

Using similar arguments one can show that the exact solution satisfies

$$\underline{A}^T\underline{B}=\underline{B}^T\underline{A} \tag{B19}$$

because the S matrix has to be symmetric. To second order this equation determines the antisymmetric part of $B^{(2)}$,

TABLE VII. Convergence of the e^--N_2 Σ_g eigenphase sum with respect to the matching radius r. Shown is the difference between the asymptotic value $\delta^\infty=2.601\,316\,4$ and the corrected and uncorrected eigenphase sums (see text). N gives the number of channels which are corrected according to Eqs. (B12) and (B13). The remaining $21-N$ channels are corrected via Eq. (B23). The scattering energy is $E=0.25$ Ry.

r (a.u.)	$(\delta^{\mathrm{corr}}-\delta^\infty)\times10^6$	$(\delta^{\mathrm{uncorr}}-\delta^\infty)\times10^6$	N
7	145.8	24923	3
8	111.9	21796	4
10	55.2	17370	5
12	31.8	14348	5
15	14.6	11182	6
20	5.2	8142	8
25	4.0	6263	10
30	1.0	4963	11
40	0.1	3366	14
50	−0.5	2403	17
60	−0.9	1749	18
80	−0.4	940	21
100	0.0	552	21
150	0.1	234	21
200	0.0	130	21

$$\underline{B}_A^{(2)}=\tfrac{1}{2}(\underline{B}^{(2)}-\underline{B}^{(2)T})=\tfrac{1}{2}(\underline{B}^{(1)T}\underline{A}^{(1)}-\underline{A}^{(1)T}\underline{B}^{(1)}) \ . \tag{B20}$$

In the actual calculations we have approximated $A^{(2)}$ and $B^{(2)}$ by $A_H^{(2)}$ and $B_A^{(2)}$, respectively.

The coefficients $q_j^{(l)}$ can become very large ($>10^6$) for large l (in particular if $l>kr$). When this happens, the numerical stability is lost. Fortunately it turns out that only the quantity

$$\mathrm{Im}(\underline{A}^{(1)}+\underline{B}^{(1)})=\frac{1}{k}\int_r^\infty dr'\underline{j}\,\underline{V}\,\underline{j} \tag{B21}$$

is of importance for correcting those channels which are closed at the matching radius r. Since the Riccati-Bessel function $j_l(kr)$ vanishes rapidly for $kr<l$ one may extend the integration (B21) to zero. We then can solve the integral analytically and define

$$c_{nll'}=\int_0^\infty j_l(kr)r^{-n}j_{l'}(kr)dr=\frac{\pi}{2}\left[\frac{k}{2}\right]^{n-1}\frac{\Gamma(n-1)\Gamma((l+l'+3-n)/2)}{\Gamma((l-l'+n)/2)\Gamma((l'-l+n)/2)\Gamma((l+l'+n+1)/2)} \ . \tag{B22}$$

For the closed channels we therefore replace Eqs. (B12) and (B13) by

$$A_{ll'}^{(1)}=B_{ll'}^{(1)}=(i/2k)\sum_n V_{nll'}c_{nll'} \ . \tag{B23}$$

The simple perturbative correction of the Jost solution leads to a quite dramatic improvement of the convergence with respect to the matching radius r. To demonstrate this improvement we have performed scattering calculations on the e^--N_2 system in Σ_g symmetry for varying matching radii r. The scattering energy was $E=0.25$ Ry and we have accounted for 21 coupled channels, i.e., $l_{\max}=40$. The second and third columns of Table VII show the difference between δ^∞ and the corrected ($\mathcal{X}=h^+A+h^-B$) and uncorrected ($\mathcal{X}=h^+$) eigenphase sum, respectively. Here, δ^∞ represents the eigenphase sum to which we assume the results converge for $r\to\infty$. Using the perturbative correction one can stop the integration at a considerably smaller value of r. The perturbative correction will be of particular importance if one studies the scattering from polar molecules.

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