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Study of electron-molecule collisions via the finite-element method and R-matrix propagation technique: Model exchange

Farzan Abdolsalami
Department of Engineering Science, Trinity University, San Antonio, Texas 78212

Mehran Abdolsalami and Pedro Gomez
Engineering Department, St. Mary's University, San Antonio, Texas 78228

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We have applied the finite-element method to electron-molecule collisions. All the calculations are done in the body frame within the fixed-nuclei approximation. A model potential, which is added to the static and polarization potential, has been used to represent the exchange effect. The method is applied to electron-H_2 scattering and the eigenphase sums and the cross sections obtained are in very good agreement with the corresponding results from the linear-algebraic approach. Finite-element calculations of the R matrix in the region where the static and exchange interactions are strong, however, has about one-half to one-fourth of the memory requirement of the linear-algebraic technique.

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The finite-element method (FEM) has been used extensively to solve problems in all areas of science and engineering. These problems, which can be very complex in nature, are commonly described by differential, integral, integrodifferential, or variational equations which are very suitable for finite-element applications [1–3]. One begins the analysis by breaking up the region of interest in the problem into small elements. Within each element, the dependent variables of the governing system equations are approximated by interpolating or trial functions such as polynomials. System equations are then transformed into linear algebraic equations in each element by substituting the assumed interpolating functions. Next, element algebraic equations are assembled together in a much larger set of algebraic equations called the system equations, which incorporate the interior boundary conditions (continuity requirements at the boundary of two adjacent elements). These algebraic equations which approximate the system equations are solved for the expansion coefficients of the dependent variables in terms of the trial functions. These expansion coefficients can be arranged to be the values of the dependent variables at every node (end points of an element), which are then obtained by solving the algebraic system equations. The global boundary conditions of the problem need to be imposed before these equations are solved, since they introduce linear constraint equations that must be added to the system equations. System equations obtained from the FEM are normally huge for complex systems, but can be solved economically because the coefficient matrices are sparse. The accuracy of the results can be improved systematically by either reducing the size of elements over which the solutions are approximated by interpolating functions, or by increasing the degree of the interpolating functions until the desired convergence is reached.

In the recent years, the FEM has been applied to quantum-mechanical problems in atomic, molecular, and solid-state physics [4–6]. For example, the FEM is very suitable to study few-body problems by means of solving the appropriate Schrödinger equation. Wave functions are approximated by interpolating functions in each element with the overall finite-element solution being accurate over the entire domain.

In this paper, we apply the FEM to study electron-molecule scattering within the rigid-rotor (RR) approximation [7]. The body-frame fixed-nuclei (BF-FN) Schrödinger equation for this problem is given by [8]

$$[\nabla^2 - 2V_{\text{int}}(\mathbf{r},\mathbf{R}) + k_0^2]\mathbf{u}(\mathbf{r},\mathbf{R}) = 0 \ , \tag{1}$$

where k_0^2 and $\mathbf{u}(\mathbf{r},\mathbf{R})$ are the energy and wave function of the scattering electron, respectively. In (1), $\mathbf{r}$ represents the position vector of the scattering electron with respect to the center of mass of the nuclei, and $\mathbf{R}$ is the vector representing the internuclear separation of the target. The interaction potential between the scattering electron and the target molecule is represented by $V_{\text{int}}(\mathbf{r},\mathbf{R})$. This potential can be written in terms of its static, polarization, and exchange components as

$$V_{\text{int}}(\mathbf{r},\mathbf{R}) = V_{\text{st}}(\mathbf{r},\mathbf{R}) + V_{\text{pol}}(\mathbf{r},\mathbf{R}) + V_{\text{ex}}(\mathbf{r},\mathbf{R}) \ . \tag{2}$$

Static potential results from the Coulomb interaction between the scattering electron and the constituent electrons and nuclei of the target molecule. This potential term is implemented here by averaging the Coulomb potential energy over the $X\,^1\Sigma_g^+$ wave function [9] to obtain $V_{\text{st}}(\mathbf{r},\mathbf{R})$.

For polarization, we use an *ab initio* potential developed by Gibson and Morrison [10]. This polarization potential $V_{\text{pol}}(\mathbf{r},\mathbf{R})$ is determined from self-consistent-field (SCF) calculations where the induced polarization is determined as the difference between two energy-optimized functionals of an adiabatic electron-molecule Hamiltonian. With the scattering electron fixed in space, these two functionals correspond to polarized and unpolarized target wave functions, respectively. The

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nonadiabatic effects are then incorporated using a nonpenetrating approximation originally introduced by Temkin [11]. The polarization potential has the asymptotic form

$$V_{\text{pol}}(\mathbf{r},\mathbf{R}) \sim -\frac{\alpha_0(\mathbf{R})}{2r^4} - \frac{\alpha_2(\mathbf{R})}{2r^4} P_2(\cos\theta) , \tag{3}$$

where $\alpha_0(\mathbf{R})$ and $\alpha_2(\mathbf{R})$ are spherical and nonspherical polarizabilities, respectively.

The exchange effect is the result of explicitly imposing the antisymmetrization requirement of the Pauli principle on the system wave function. In this calculation, we use an approximate treatment of the exchange effect which simplifies the computation. The particular model potential used is a variant of the free-electron-gas (FEG) potential originally proposed by Hara [12]. In this model exchange potential, we treat the ionization potential of the neutral target I as a parameter. The resulting tuned free-electron-gas (TFEG) potential [10] can be simply added to the static and polarization components of the interaction potential. The tuning procedure is carried out in the BF-FN formulation within the static-exchange approximation, in which induced-polarization effects are neglected. This procedure requires knowledge of eigenphase sum [13] in one symmetry at one energy from an exact-static-exchange calculation, in which integro-differential BF-FN radial scattering equations are solved [14].

The interaction potential can be expanded in terms of Legendre polynomials as

$$V_{\text{int}}(\mathbf{r},\mathbf{R}) = \sum_{\lambda} v_{\lambda}(r,\mathbf{R}) p_{\lambda}(r,\theta) , \tag{4}$$

where $v_{\lambda}(r,\mathbf{R})$ is an expansion coefficient which can be used to generate the potential matrix elements in the FEM analysis of the radial BF-FN Schrödinger equation as described below.

The BF-FN Schrödinger equation involves the vector $\mathbf{r}$. This equation can be transformed into a set of coupled differential equations of variable r by expanding the wave function $\mathbf{u}(\mathbf{r},\mathbf{R})$ in terms of spherical harmonics $Y_l^{\Lambda}(\hat{r})$ as

$$\mathbf{u}(\mathbf{r},\mathbf{R}) = \sum_{l} \frac{1}{r} u_l^{\Lambda}(r,\mathbf{R}) Y_l^{\Lambda}(\hat{r}) , \tag{5}$$

where Λ is the projection of the angular momentum along the internuclear axis ($\hat{z}$ axis). Substituting (5) into (1) gives [15]

$$\left[\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k_0^2\right] u_{ll_0}^{\Lambda}(r,\mathbf{R}) = 2\sum_{l'} V_{ll'}(r,\mathbf{R}) u_{l'l_0}^{\Lambda}(r,\mathbf{R}) , \tag{6}$$

which is the standard BF-FN radial equation. In this equation k_0^2 represents the initial energy of the scattering electron, l is the orbital angular momentum of the scattering electron, and l_0 designates a particular linearly independent solution. The coupling matrix elements $V_{ll'}(r,\mathbf{R})$ are evaluated at internuclear separation $\mathbf{R}$ in terms of the Legendre expansion coefficients $v_{\lambda}(r,\mathbf{R})$ as

$$V_{ll'}(r,\mathbf{R}) = \sum_{\lambda} g_{\lambda}(ll';\Lambda) v_{\lambda}(r,\mathbf{R}) , \tag{7}$$

where the angular-coupling coefficients are [16]

$$g_{\lambda}(ll';\Lambda) = (-1)^{\Lambda} \frac{[(2l+1)(2l'+1)}{2\lambda+1} \times C(l,l',\lambda;0,0,0) C(l,l',\lambda;-\Lambda,\Lambda,0) . \tag{8}$$

In (8), $C(l,l',\lambda;0,0,0)$ represents the appropriate Clebsh-Gordan [17] coefficient. The BF-FN K matrix $K^{\Lambda}(\mathbf{R})$ is obtained by imposing on the solutions of (6) the K-matrix boundary conditions [18]

$$u_{ll_0}^{\Lambda}(r;\mathbf{R}) \sim \delta_{ll_0} \hat{j}_{l_0}(k_0 r) - K_{ll_0}^{\Lambda}(\mathbf{R}) \hat{n}_l(k_0 r), \quad r \to \infty , \tag{9}$$

where $\hat{j}_l(k_0 r)$ and $\hat{n}(k_0 r)$ are the Ricatti Bessel and Neumann functions, and δ_{ll_0} is the Kronecker delta function. The partial cross sections can be obtained from the equation

$$\sigma^{\Lambda}(\mathbf{R}) = \frac{\pi}{k_0^2} \sum_{ll_0} |T_{ll_0}^{\Lambda}(\mathbf{R})|^2 , \tag{10}$$

where the T matrix is given by

$$T^{\Lambda}(\mathbf{R}) = 2K^{\Lambda}(\mathbf{R})[I - iK^{\Lambda}(\mathbf{R})]^{-1} . \tag{11}$$

In the R-matrix propagation technique, we seek an alternative solution $g_{ll_0}(r,\mathbf{R})$ to Eq. (6) defined by [15]

$$u_{ll_0}(r,\mathbf{R}) = \sum_{\bar{l}} g_{l\bar{l}}(r,\mathbf{R}) \frac{\partial u_{\bar{l}l_0}(r=a,\mathbf{R})}{\partial r} . \tag{12}$$

Here $r=a$ defines the maximum radial distance occupied by most of the charge cloud of the molecules, where the static and exchange interactions are strong. The R-matrix boundary conditions imposed on $g_{ll_0}(r,\mathbf{R})$ are clear from Eq. (12). At $r=0$, $g_{ll_0}(r,\mathbf{R})$ is the zero matrix and at $r=a$, $[\partial g_{ll_0}(r=a,\mathbf{R})]/\partial r$ is the identity matrix. Since g_{ll_0} $(r=a,\mathbf{R})$ is just the R matrix, it can be propagated into the asymptotic region to find the K matrix and scattering cross sections [19].

In this paper, we apply the FEM to electron molecule scattering, assuming R-matrix boundary conditions. These boundary conditions have a clear advantage over the K-matrix boundary conditions in memory usage, as discussed below. We compare our results with those obtained from the linear-algebraic (LA) approach [15], and show that for 1% accuracy, the finite-element code requires far less memory than the LA code. The justification for using the LA approach for comparison is as follows: this technique is one of the few that can implement exchange exactly. The significant memory advantage of the FEM over the LA approach when implementing model exchange is the motivation to believe that once exact exchange is implemented into the finite element code, it still requires far less memory than the LA code. Even though the sparsity of the system matrix in the FEM is lost when exact exchange is introduced due to the coupling of the wave function at different points, our preliminary studies show that the FEM requires fewer meshes to compute the R matrix in the region of interest, resulting in a smaller system of equations to solve.

In what follows, we first discuss the finite-element implementation of the BF-FN radial equation and its appropriate K- and R-matrix boundary conditions. Next, the eigenphase sums and the scattering cross sections obtained from the finite-element and LA approaches, with both implementing R-matrix boundary conditions, will be compared. Finally, the clear advantage of the FEM in memory usage because of the sparsity and smaller size of its system of equations will be covered.

The finite-element model applied to this problem is based on the Galerkin method [1]. The wave function $u_{ll_0}(r,\mathbf{R})$ in any element is approximated by [20]

$$u_{ll_0}(r)=\sum_{\alpha=1}^{2}[\phi_\alpha(x)u_\alpha+\bar{\phi}_\alpha(x)\bar{u}_\alpha],\quad 0\le x\le 1\ , \tag{13}$$

where

$$\phi_\alpha(x)=\begin{cases}2x^3-3x^2+1, & \alpha=1\\ 3x^2-2x^3, & \alpha=2\end{cases} \tag{14}$$

and

$$\bar{\phi}_\alpha(x)=\begin{cases}x^3-2x^2+x, & \alpha=1\\ x^3-x^2, & \alpha=2\end{cases} \tag{15}$$

define the basis for the expansion of the wave function in every element. In Eq. (13), $x=0$ and 1 represent the end points of any element with the actual radial distance r within an element given by $r=(n-1)h+hx$, where n is the element index and h is the mesh size. These definitions force u_α and $\bar{u}_\alpha$ to be the values of the wave function and its derivative at the end points of an element $(x=0,1)$.

To implement the FEM using K-matrix boundary conditions, we multiply Eq. (6) by each of the basis functions ϕ_α and $\bar{\phi}_\alpha$, and integrate in the range 0 to $r_{\max}$, where $r_{\max}$ is the radial distance beyond which the asymptotic behavior of the wave function is assumed to be valid. We now have

$$\int_0^{r_{\max}}\left\{\left[\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}+k_0^2\right]u^{\Lambda}_{ll_0}(r)\right.$$
$$\left.-2\sum_{l'}V_{ll'}(r)u^{\Lambda}_{l'l_0}(r)\right\}\phi_i(x)dr=0\ , \tag{16}$$

where $\phi_i(x)$ $(i=1,4)$ represents any of the basis functions ϕ_α and $\bar{\phi}_\alpha$.

The integral in (16) can now be discretized into N small elements, and within each element $u_{ll_0}(r)$ is approximated by Eq. (13). Once each integral over an element is evaluated, the results can be added together to obtain the linear homogeneous equations $\mathbf{AU}=\mathbf{0}$ which approximate Eq. (6). The size of the square coefficient matrix $\mathbf{A}$ is $(2N+2)m$, where N is the total number of elements in the finite-element analysis, and m is the number of coupled equations. Matrix $\mathbf{A}$ is sparse and can be divided into m^2 partitions of diagonal matrices with a bandwidth of 3. Each partition would then represent the contribution of one of the radial wave functions $u_{ll_0}(r)$ to the overall set of coupled differential equations. Implementing the boundary condition of Eq. (9) gives an additional set of nonhomogeneous equations from which the K matrix can be found. This matrix is then used to find the scattering cross sections and eigenphase sums for the

TABLE I. Calculated values of the scattering cross sections in square bohr (top line) and eigenphase sums in radians (lower line) from the finite-element and linear-algebraic techniques. All the results shown are based on five channels with $r=a$ set to 10 bohr. This table shows that for all symmetries, the results obtained from these two methods are in agreement to within less than 1%.

	Σ_g		Σ_u		Π_g		Π_u		Total	
(eV)	LA	FEM	LA	FEM	LA	FEM	LA	FEM	LA	FEM
0.047	33.178	33.452	0.394	0.394	0.012	0.012	0.016	0.016	33.600	33.874
	(−0.094)	(−0.094)	(0.011)	(0.011)	(0.001)	(0.002)	(0.002)	(0.002)	(0.108)	(0.109)
0.070	34.588	34.864	0.506	0.505	0.015	0.015	0.035	0.035	35.144	35.419
	(−0.117)	(−0.117)	(0.015)	(0.015)	(0.002)	(0.003)	(0.003)	(0.003)	(0.137)	(0.137)
0.100	35.953	36.230	0.650	0.650	0.018	0.018	0.067	0.067	36.688	36.964
	(−0.142)	(−0.142)	(0.021)	(0.021)	(0.003)	(0.003)	(0.005)	(0.005)	(0.171)	(0.171)
0.500	41.874	42.129	2.866	2.854	0.050	0.045	0.743	0.742	45.533	45.775
	(−0.344)	(−0.345)	(0.098)	(0.097)	(0.011)	(0.011)	(0.038)	(0.038)	(0.491)	(0.491)
1.000	42.438	42.656	6.198	6.164	0.086	0.086	1.693	1.690	50.415	50.596
	(−0.497)	(−0.498)	(0.202)	(0.201)	(0.021)	(0.021)	(0.080)	(0.080)	(0.800)	(0.800)
3.000	35.778	35.886	16.038	15.946	0.224	0.223	4.209	4.201	56.249	56.257
	(−0.849)	(−0.851)	(0.585)	(0.583)	(0.057)	(0.057)	(0.216)	(0.216)	(1.707)	(1.707)
5.000	28.723	28.778	16.849	16.772	0.344	0.343	4.860	4.849	50.776	50.742
	(−1.051)	(−1.053)	(0.817)	(0.815)	(0.090)	(0.090)	(0.306)	(0.305)	(2.264)	(2.263)
7.000	23.231	23.256	14.846	14.796	0.438	0.436	4.725	4.714	43.240	43.202
	(−1.190)	(−1.192)	(0.946)	(0.944)	(0.121)	(0.120)	(0.364)	(0.346)	(2.621)	(2.620)

electron molecule system.

The finite-element implementation of the R-matrix boundary conditions is similar to the previous case, except that the upper limit of the integral in Eq. (16) is $r=a$. Since $r=a$ is at least one order of magnitude smaller than $r_{\max}$, the finite element implementation of the R-matrix boundary conditions require far less computer memory than the K-matrix boundary conditions.

We have applied the FEM to electron-H_2 scattering using the R-matrix boundary conditions. Table I shows the cross sections and eigenphase sums obtained using this method and the corresponding results from the LA approach. In both calculations, we have used five channels with $r=a$ set to 10 bohr. The energy range used for comparison is 0.047–7.0 eV. For all energies, the number of elements used in the FEM analysis is 14, with two equally spaced elements in each of the following intervals of r: 0–0.7, 0.7–1.5, 1.5–2.5, 2.5–4.0, 4.0–6.0, 6.0–8.0, and 8.0–10.0. The mesh size obtained in each subdomain (0.35, 0.4, 0.5, 0.75, 1.0, 1.0, and 1.0) represents the maximum value allowed to obtain stable results. Increasing the number of meshes in the FEM analysis beyond 14 and thereby reducing the step sizes does not change the cross sections, implying that convergence is achieved. From Table I, it is clear that the results obtained from the FEM and LA approaches are in agreement to within less than 1% for all energies. All the results shown in this table are computed on a sparcstation 2 with 20 Mb of memory. The average CPU time required to obtain the cross sections for a given energy and symmetry using the FEM and LA codes is less than 20 s. To obtain the R matrix in the region of strong static and exchange interactions, the finite-element code requires a system matrix of size 150 with a density of 17%. the LA code, on the other hand, results in a full matrix of size 275. Using the standard IMSL (International Mathematical Statistical Libraries) routines to solve the appropriate system equations require 2–4 times more memory for the LA code compared to the finite-element code [21]. As a result, for large molecules, where the number of channels and/or effective radii for the static and exchange potentials increases significantly, the LA approach has the disadvantage of requiring far more storage.

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[20] From now on, we suppress the **R** coordinate in $u_{ll_0}(r,\mathbf{R})$ and $V_{ll_0}(r,\mathbf{R})$ to simplify notation. This will not introduce any problem since we use the rigid rotor approximation which makes **R** a parameter fixed at its equilibrium value.

[21] The system equations obtained from the finite-element code are solved using a real sparse linear equation solver available in IMSL routines.