

Cross sections for the elastic scattering of low-energy electrons by molecular fluorine: an approximate theoretical treatment using discrete basis functions†

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Abstract. We present phaseshifts and total cross sections for the elastic scattering of low-energy (0–13.6 eV) electrons by molecular fluorine. The phaseshifts are obtained by an approximate technique based on the weak asymptotic coupling of orbital angular momenta and are calculated solely from the results of a discrete basis set diagonalization of the molecular Hamiltonian. Correlation and polarization effects are not treated. The elastic cross section is dominated by a Σ_u^- shape resonance at about 2.2 eV in the static-exchange model.

1. Introduction

In a previous paper (McCurdy *et al* 1976, hereafter referred to as I) we outlined a method for obtaining approximate low-energy electron–diatomic-molecule elastic scattering cross sections solely from the results of a basis set Hartree–Fock calculation on the closed-shell molecular target. The method was based on the assumed validity of the so-called ‘low *l*-spoiling’ approximation (Fano 1970) of low-energy electron–molecule scattering, as well as the fact that the eigenfunctions at scattering energies obtained by diagonalizing the Hamiltonian in a sufficiently large set of square-integrable basis functions are, apart from an overall normalization, equal to the true wavefunctions over the region spanned by the basis set (Hazi and Taylor 1970, Hazi and Fels 1971). These assumptions were tested by calculations on e^- – H_2 and e^- – N_2 and the results obtained were found to be in reasonably good agreement with more elaborate theoretical treatments. In this paper, the method of I is applied to a study of low-energy e^- – F_2 elastic scattering.

Very little is known about the scattering of electrons by F_2 , either experimentally or theoretically. To our knowledge, no previous theoretical studies of elastic e^- – F_2 scattering have been performed. A rigorous treatment would be complicated by the

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fact that the ground state of F_2 is more difficult to describe accurately than the ground states of other first-row diatomics. The calculations presented here make use of the static-exchange approximation in which the F_2 target is frozen in its Hartree–Fock ground-state wavefunction. The well known failure of the Hartree–Fock wavefunction to predict F_2 to be bound relative to two fluorine atoms (Wahl 1964) raises some doubt as to the adequacy of a Hartree–Fock description for constructing a scattering potential. Thus, until more accurate calculations are performed, the present results should be considered preliminary.

Our calculations on this system incorporate a number of simplifying approximations. As in the computations reported in I, we have ignored correlation and polarization effects in restricting ourselves to a study of the static-exchange approximation with a Hartree–Fock target wavefunction. The dominant feature we find in the total elastic cross section is a Σ_u^+ shape resonance coming from the $p\sigma$ phaseshift at about 2.2 eV. Before presenting our results, we give a brief summary of the procedure used in this work.

2. Theory

The method used to obtain electron–diatomic-molecule phaseshifts, as well as the nature and validity of the assumptions underlying the method, have been discussed fully in I and only a brief summary will be given here. Simply stated, the low l -spoiling assumption states that at low electron energies orbital angular momentum is approximately conserved in the body-fixed molecular frame. This conservation comes about from the repulsive centrifugal barrier of the effective potential which effectively prevents slow electrons from penetrating the highly non-spherical molecular core (Fano 1970). It was further argued that this approximation should hold particularly well for a homonuclear diatomic molecule, since in this case the centre of symmetry causes even values of l to uncouple from odd values.

We stress that the low l -spoiling approximation does not imply that the continuum wavefunction is proportional to a particular spherical harmonic at small radial distances nor that a single-centre expansion of the molecular potential or the scattering wavefunction is rapidly convergent. It merely states that at low energies it should be possible to find continuum solutions asymptotically proportional to a particular partial wave.

To this end, we diagonalize the molecular Hamiltonian in a discrete set of Gaussian basis functions that give a non-vanishing contribution to the particular symmetry (labelled by l and $|m|$ values) under consideration. This set is chosen to give a good description of the occupied Hartree–Fock molecular orbitals and is then augmented with additional diffuse functions of one particular symmetry, most of which are placed at the centre of the molecule. The molecular Hamiltonian is then diagonalized in this basis. For each positive energy eigenfunction, $\Psi_E(\mathbf{r})$, a radial wavefunction $R_{lm}^E(r)$ is obtained by projection with the appropriate spherical harmonic:

$$R_{lm}^E(r) = \int d\Omega Y_{lm}^*(\Omega) \Psi_E(\mathbf{r}). \quad (1)$$

For the particular case of a diatomic molecule with Gaussian basis functions chosen along the axis of symmetry the projection integral of equation (1) can be done analytically.

On the assumption that the basis set representation of $R_{lm}^E(r)$ is valid over the region spanned by the basis (Hazi and Taylor 1970, Hazi and Fels 1971), and that this region is sufficiently large to reach a point where the potential has become vanishingly small, the tangent of the phaseshift may be obtained by plotting

$$\tan \delta_{lm}(r) = -\frac{kR_{lm}^E(r)j_l'(kr) - R_{lm}^{E'}(r)j_l(kr)}{kR_{lm}^E(r)n_l'(kr) - R_{lm}^{E'}(r)n_l(kr)} \quad (2)$$

as a function of r and extracting a value for the phaseshift from the region where this function levels off to a constant value. This part of the procedure can be thought of as a basis set approach to the familiar variable-phase method of potential scattering (Calogero 1967). In contrast to the latter procedure, however, the value of $\tan \delta_{lm}(r)$ obtained from equation (2) will again vary as a function of r when the basis is no longer capable of representing $R_{lm}^E(r)$ accurately.

The assumption of angular momentum decoupling simplifies the problem considerably since we do not have to face the prospect of dealing with more than one linearly independent regular solution at one energy for a particular choice of l and m . Relaxation of this assumption would complicate the problem considerably (Hazi 1973).

3. Results

All of our calculations were carried out at the equilibrium internuclear separation of F_2 , $2.68 a_0$. Correlation and polarization effects have not been considered in these computations; that is, the continuum wavefunctions were obtained as the positive energy eigenfunctions of the Hartree-Fock Hamiltonian of F_2 . The HF occupied orbitals for F_2 were computed using a basis of [6s/5p] Gaussians on each fluorine contracted from a (10s/6p) set of primitives similar to that suggested by Dunning (1970), plus two $d\sigma$ and two $d\pi$ polarization functions (Dunning 1971) on each fluorine. The results of the self-consistent field (SCF) computation are summarized in table 1.

Five separate diagonalizations were performed to obtain virtual Hartree-Fock eigenfunctions of Σ_g^+ , Σ_u^+ , Π_u , Π_g and Δ_g symmetry. For the Σ_g^+ orbitals, the previous basis was augmented by two s-type and two z-type Gaussians on each fluorine and eight more s functions at the midpoint. The Σ_u^+ calculations were done by adding

Table 1. SCF molecular orbital eigenvalues for F_2^\dagger . (Energies are given in au.)

E_{HF}	-198.73201
$\epsilon_{1\sigma_g}$	-26.4129
$\epsilon_{2\sigma_g}$	-1.7523
$\epsilon_{3\sigma_g}$	-0.7383
$\epsilon_{1\sigma_u}$	-26.4126
$\epsilon_{2\sigma_u}$	-1.4890
$\epsilon_{1\pi_u}$	-0.7984
$\epsilon_{1\pi_g}$	-0.6563

† In a 6s/5p basis of contracted Gaussian functions. This basis was only used to represent the *occupied* orbitals.

Table 2. e^- -F₂ phaseshifts.

s		pσ		pπ		dπ		dδ	
k(au)	δ ₀₀	k(au)	δ ₁₀	k(au)	δ ₁₁	k(au)	δ ₂₁	k(au)	δ ₂₂
0.0216	3.1005	0.0258	0.00001	0.0376	3.14143	0.0460	3.1415917	0.3880	0.07
0.04619	3.054	0.0480	0.0001	0.0699	3.14078	0.0804	3.141589	0.5639	0.20
0.07738	2.994	0.0736	0.002	0.1110	3.1377	0.1239	3.141534	0.8155	0.22
0.1199	2.914	0.1147	0.004	0.1671	3.1308	0.1838	3.14135	1.138	0.38
0.1806	2.798	0.1684	0.044	0.2469	3.105	0.2692	3.1395	1.614	0.49
0.2695	2.644	0.2430	0.09	0.3636	3.054	0.3922	3.132		
0.4021	2.40	0.3380	0.32	0.5394	2.895	0.5714	3.090		
0.5973	2.10	0.4210	1.73	0.8039	2.78	0.8358	2.976		
0.903	1.75	0.572	2.32	1.139	2.5	1.1236	2.75		
1.086	1.69	0.749	2.49						
		1.170	2.25						

two s and one z function on the fluorines and nine more z functions at the midpoint to the HF basis. For the Π_u calculations, one x-type Gaussian on each fluorine and eight more at the midpoint were added to the HF basis; one additional x function on the fluorines and twelve more xz-type Gaussians at the midpoint were used in the Π_g diagonalization. The Δ_g basis consisted of the HF basis plus six xy Gaussians on each fluorine plus eight more at the midpoint.

Table 2 lists the s, pσ, pπ, dπ and dδ phaseshifts and corresponding eigenvalues. The number of digits given in the phaseshifts represents the number of significant digits that could be deduced from a region over which the phaseshift had stabilized. These figures merely reflect the stability of the extraction procedure and do not indicate the possible convergence of the phaseshift with respect to basis functions.

Since the eigenvalues corresponding to different symmetries cannot be made to coincide by a simple diagonalization of the Hamiltonian, the computed phaseshifts must be interpolated before cross sections can be calculated. These interpolated values were used to compute a total elastic cross section which satisfies the equation

$$\sigma_{\text{tot}} = \frac{4\pi}{k^2} \sum_{l,m} \sin^2 \delta_{lm}. \quad (3)$$

The total cross section is depicted in figure 1.

The cross section is seen to be dominated by a Σ_u^+ -pσ resonance at about 2.2 eV and rises from a background value of approximately $40 a_0^2$ to almost $120 a_0^2$ over an energy range of about 0.8 eV. Unfortunately, there were only five computed eigenvalues in the interesting region over which the pσ phaseshift rises through 2.4 rad, and thus the resonant cross section will be somewhat sensitive to the way in which the phaseshifts are interpolated.

4. Discussion

We have applied a simple, but approximate, method to calculate low-energy e^- -F₂ elastic cross sections. The calculations were carried out under the assumption of low l-spoiling and correlation and polarization effects were also ignored. Since the method is based solely on the diagonalization of the molecular Hamiltonian over

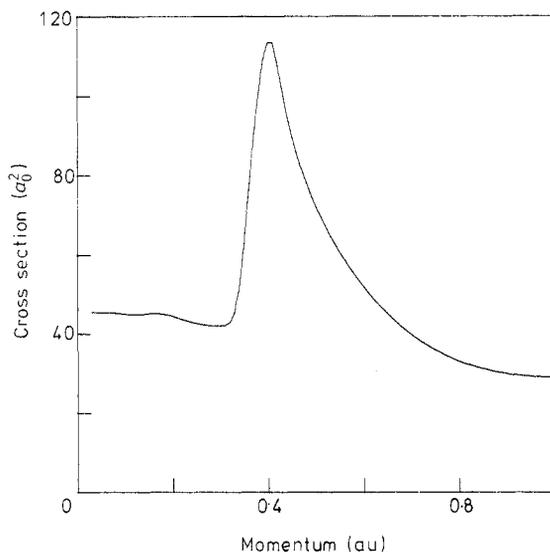


Figure 1. e^- - F_2 total elastic cross sections obtained from interpolated phaseshifts.

a discrete set of Gaussian basis functions and asymptotic boundary conditions are not explicitly imposed, the entire procedure was implemented with standard bound-state molecular programs. Total cross sections were found by interpolation of phaseshifts obtained at discrete energy eigenvalues. The dominant feature we find in the elastic cross section is a 2.2 eV Σ_u^+ shape resonance coming from the $p\sigma$ partial wave.

However, it is entirely possible that this resonance is an artifact of the static-exchange approximation and would disappear if correlation effects were included. It is interesting to note that a comparison of the Hartree-Fock potential energy curves for the ground states of F_2 (Das and Wahl 1966) and F_2^- (Gilbert and Wahl 1971) suggests that F_2^- is stable with respect to F_2 and a free electron at the equilibrium internuclear distance of F_2 . If that were the case, the shape resonance found in the present static-exchange calculation would be of doubtful validity. However, if a multiconfiguration, self-consistent field (MCSCF) potential energy curve for F_2 (Das and Wahl 1972) is used in the above comparison, F_2^- is predicted to be unstable at the equilibrium internuclear distance of F_2 . Experimental evidence for the resonance may be inferred from studies on the dissociative attachment of low-energy electrons to F_2 ; this work is summarized in a review by Caledonia (1975). The measured rate constants for DA to F_2 are quite large, indicating that the reaction may well proceed through resonance excitation to an unbound F_2^- ion. In any event, the possibility of a stable negative ion suggests that the static-exchange approximation may be less valid for electron- F_2 scattering than for the previously studied cases of e^- - H_2 and e^- - N_2 (McCurdy *et al* 1976). Since there are no other calculations or experiments with which to compare these results directly, confirmation of our findings must await further study. One important question that must be answered is whether, in view of the poor HF description of F_2 , the use of a correlated F_2 ground state in the static-exchange approximation would significantly modify these results. Work along these lines is presently under study.

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