

Correlation effects in R -matrix calculations of electron- F_2 elastic scattering cross sections

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Correlation effects are studied in electron scattering off the fluorine molecule. Fixed-nuclei approximation R -matrix calculations of the elastic collision cross sections are presented for a set of internuclear distances at three levels of correlation. The aim of this work is to study the role of electronic correlation on the properties of the $^2\Sigma_u$ resonance. The Feshbach-Fano R -matrix method of resonance-background separation is used to study the effect of inclusion of various levels of correlation on the energy and width of the $^2\Sigma_u$ resonance. Data required for construction of the nonlocal resonance model (construction of a discrete state and its coupling to the continuum) which allows the calculation of inelastic processes such as dissociative electron attachment and vibrational excitation [W. Domcke, Phys. Rep. **208**, 97 (1991)] including the correlation are presented. © 2007 American Institute of Physics. [DOI: [10.1063/1.2789430](https://doi.org/10.1063/1.2789430)]

I. INTRODUCTION

Understanding of the electron-molecule collisions is important for determining the energy balance and transport properties of electrons in low-temperature gases and plasmas under variety of conditions. Important applications of these processes include thermonuclear fusion, astrophysics, physics of upper atmosphere layers of planets as well as technological applications connected with laser physics or surface physics. In this context it is desirable to study electron scattering off the fluorine molecule. It plays an important role in the determination of properties of the electron-beam energized fluoride excimer lasers as well as in other applications.¹

Significant progress has been made in development of quantum scattering theory methods for resonant electron-molecule collisions based on *ab initio* methods of quantum chemistry. Recently, particular attention was paid to application of the Feshbach-Fano projection formalism,² the complex absorbing potential (CAP) method,^{3,4} complex rotation method⁵ as well as to the R -matrix theory⁶ and several others. All of them have been successfully applied to electron scattering off polyatomic molecules. In particular, method for combining the Feshbach-Fano formalism with the R -matrix method (called Feshbach-Fano R -matrix) has been developed and successfully applied to the separation of resonances in the potential scattering⁷ as well as in the electron-molecule collisions.⁸⁻¹⁰ This method enables the extraction of the discrete state and its coupling to the background continuum on the basis of the standard R -matrix calculations. From these quantities it is possible to construct the nonlocal resonance model (NRM) used to study the processes connected with the nuclear dynamics such as dissociative electron attachment (DEA), associative electron detachment, and vibrational excitation (VE).^{11,12}

The electron scattering off fluorine molecule has been investigated theoretically several times. The first *ab initio* calculation of DEA and VE has been carried out by Hazi *et al.*¹³ using the method developed by O' Malley.¹⁴ In this calculation the correlation has been included on the level of configuration interaction (CI) expansion consisting of very restricted number of configurations. Moreover, this calculation did not give the relative position of the potential curve of the neutral target and negative ion. Subsequent R -matrix study of elastic electron collision with the F_2 molecule by Morgan and Noble¹⁵ has included the correlation on the level of the static exchange with polarization (SEP). This study found that the ionic state is stable against autodetachment at the equilibrium internuclear separation of the neutral molecule. Another calculation of the potential energy curve of the $X^2\Sigma_u^+$ resonance by Ingr *et al.*¹⁴ made use of the CAP/CI method. This calculation treats the correlation by the multi-reference CI (MRCI) method. The crossing point of the neutral target potential curve with the resonance state potential curve is determined by the extrapolation of the resonance width to zero. This calculation does not provide the energy-dependent width function as required for NRM. Brems *et al.*¹¹ studied the DEA and VE of the F_2 molecule using the R -matrix method with Feshbach-Fano R -matrix (FFR) separation of the discrete state. This discrete state and its coupling with the background continuum have been used to construct the NRM and to study the nuclear dynamics processes. The R -matrix calculation has been provided using the code of Nestmann *et al.*⁶ at the SEP level of correlation. This calculation indicates that the position of the crossing point of the ionic and neutral potential curves, which is strongly influenced by the correlation included in the fixed-nuclei calculation, is of particular importance in the nuclear dynamics calculation.

The implementation of the R -matrix method by Nestmann *et al.* enables the static exchange (SE) and SEP ap-

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proach to the correlation. Recently this code has been extended in order to allow single and double excitations multireference CI (Ref. 17) (SD-MRCI) treatment of the correlation. This enables us to compare the scattering calculations on different levels of correlation and to study correlation effects in the subsequent FFR separation. The main aim of this work is to test the SD-MRCI approach in the electron scattering off the fluorine molecule studied previously on the SEP level and to study the correlation effects in the FFR separation.

This paper is organized as follows: The R -matrix theory is briefly reviewed in Sec. II A and different models of correlation included are discussed in Sec. II B. The FFR formalism is briefly summarized in Sec. II C. Technical details of the calculations are explained in Sec. III, and results obtained on different levels of correlation are discussed in Sec. IV.

II. THEORY

A. R -matrix theory

The basic idea of the R -matrix method is the division of the coordinate space into two regions separated by a sphere Ω with center in the center of mass of the molecule. Its radius r_Ω is chosen so that for scattering problem it is possible to neglect the exchange interaction between the projectile and the target molecule electrons outside the sphere, where their interaction is treated as the movement of the scattered electron in an average single particle potential.

In the fixed-nuclei approximation H_{N+1} is the $(N+1)$ -particle electronic Hamiltonian. The scattering process is described by the time-independent Schrödinger equation

$$H_{N+1}\Psi_E = E\Psi_E, \quad \Psi_E = \sum_k \Psi_k A_{Ek}, \quad (1)$$

where Ψ_k are basis functions, which can be written in the form of the close coupling expansion

$$\begin{aligned} \Psi_k(\mathbf{x}_1, \dots, \mathbf{x}_{N+1}) \\ = A \sum_{ijlm} c_{ijlm} \bar{\Phi}_{ilm}(\mathbf{x}_1, \dots, \mathbf{x}_N, \hat{\mathbf{r}}_{N+1} \sigma_{N+1}) \frac{u_{ilm}(r_{N+1})}{r_{N+1}}, \end{aligned} \quad (2)$$

where $u_{ilm}(r_{N+1})$ represent set of molecular orbitals (MOs) of the target molecule and continuum orbitals (COs). The channel functions $\bar{\Phi}_{ilm}$ in Eq. (2) are formed by coupling the target wave functions Φ_i with the spin-angle functions of the scattered electron $Y_l^m(\vartheta_{N+1}, \varphi_{N+1})s(\sigma_{N+1})$, and $\mathbf{x}_n = (\mathbf{r}_n, \sigma_n)$ denote the space and spin electron coordinates. The multi-index $\chi = \{i, l, m\}$ defines the scattering channel. The antisymmetry of the functions Ψ_k with respect to changes of all the spatial electronic coordinates is ensured by the antisymmetrization operator A . Finally, the expansion coefficients c_{ijlm} in Eq. (2) are obtained by solving the equation

$$(H_{N+1} + L_{N+1})\Psi_k = E_k \Psi_k \quad (3)$$

in the inner region. The Bloch operator¹⁸

$$L_{N+1} = \sum_{i=1}^{N+1} \frac{1}{2} \delta(r_i - r_\Omega) \left(\frac{d}{dr_i} + \frac{1}{r_i} \right) \quad (4)$$

guarantees the hermicity of the modified Hamiltonian $H_{\Omega, N+1} = H_{N+1} + L_{N+1}$ in the inner region.

Equation (1) is solved formally in the inner region⁶ using the basis [Eq. (2)] and its solutions are projected onto the channel functions $\bar{\Phi}_{ilm}$. This gives for the radial wave functions of the projectile $w_{ilm}(r)$ on the sphere

$$w_{ilm}(r_\Omega) = \sum_{i'l'm'} R_{ilmi'l'm'}(E) r_\Omega \left. \frac{dw_{i'l'm'}(r)}{dr} \right|_{r=r_\Omega}, \quad (5)$$

where the R -matrix is defined by

$$R_{ilmi'l'm'}(E) = \frac{1}{2r_\Omega} \sum_k \frac{\langle \bar{\Phi}_{ilm} | \Psi_k \rangle' \langle \Psi_k | \bar{\Phi}_{i'l'm'} \rangle'}{E_k - E} \Bigg|_{r_{N+1}=r_\Omega}. \quad (6)$$

The primes mean that the integration is carried over all the coordinates except the radial coordinate r_{N+1} .

The form of the solution in the outer region differs from Eq. (2) by the absence of the antisymmetrization operator A only (since the exchange interaction is negligible). Substitution of this solution into the Schrödinger equation (1) and projection onto the channel functions yield the system of coupled second-order differential equations

$$\begin{aligned} \left(\frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + 2(E - E_i^N) \right) w_{ilm}(r) \\ = 2 \sum_{j'l'm'} V_{ilmj'l'm'}(r) w_{j'l'm'}(r), \end{aligned} \quad (7)$$

where E_i^N is the target energy and $V_{ilmj'l'm'}(r)$ is given by the interaction potential between the target and projectile.⁶ The scattering wave function in the outer region is obtained by solving this system with boundary condition (5) providing the correct connection between the solutions in the inner and outer regions. All the scattering information can be obtained from the asymptotic form of the solutions $w_{ilm}(r)$ in the outer region by application of standard methods of scattering theory.

B. Different models of correlation

In the SE approximation no correlation is introduced in the scattering system. The R -matrix basis set is written in the form (2), where Φ_0 is the Hartree-Fock determinant $|\Phi_0\rangle$ consisting of lowest N spin orbitals (a, b, \dots) . $u_{ilm}(r)/r$ are the virtual MOs (k, l, \dots) and COs (u, v, \dots) in the symmetry of the interest. Higher eigenstates Φ_i , $i > 0$ are not taken into account.

The SEP approximation introduces the correlation between the molecule as a whole and the projectile, but not inside the molecular target. The SE space of configurations is augmented by states with singly excited target and scattered electron in virtual MO. In this approximation the R -matrix basis states can be written in the following form:

$$|\Psi_a\rangle = \sum_k c_{ka} |\Phi_0 k\rangle + \sum_u c_{ua} |\Phi_0 u\rangle + \sum_{bkl} c_{bkla} |\Phi_b^k l\rangle. \quad (8)$$

The matrix elements (The subscript int denotes that the integration is carried over the inner region.) $\langle \Psi_a | H_{N+1} | \Psi_b \rangle_{\text{int}}$ of the R -matrix Hamiltonian in this basis contain terms corresponding to the $(N+1)$ -electron Hartree-Fock (HF) Hamiltonian, terms corresponding to the correlation between the projectile and the target electrons as well as terms of form $\langle \Phi_a^k | H_{N+1} | \Phi_b^l \rangle_{\text{int}} = \langle kb || al \rangle_{\text{int}}$ introducing the additional correlation into the target. These elements are also present in the calculation of the N -electron neutral target ground state wave function in the basis set containing the $|\Phi_0\rangle$ and all the monoexcitations $|\Phi_a^k\rangle$, but according to the Brillouin theorem they do not contribute to the $|\Phi_0\rangle$ energy due to the fact that off-diagonal elements of the Fock operator are zero. On the other hand, in the $(N+1)$ -electron calculation these elements contribute to the R -matrix poles E_k . This difference in the correlation treatment of the neutral target and the scattering system causes incorrect relative positions of the R -matrix poles with respect to the HF ground state energy of the neutral-target molecule.

The CI level of the correlation treatment introduces the correlation into the target in addition to the correlation between the projectile and the target. The target wave functions Φ_i in expansion [Eq. (2)] take the form of the MRCI expansion consisting of the single and double excitations from selected references into the virtual MOs. Inclusion of the double excitations improves the behavior of the wave functions for internuclear distances, where the target is not described correctly by single-determinant wave function.

C. Feshbach-Fano R -matrix

In the following we give a brief survey of the FFR method extensively discussed by Nestmann⁸ and Kolorenč *et al.*⁷

The projection formalism developed by Feshbach^{2,19,20} provides separation of the Hilbert space of the scattering problem into the resonance scattering subspace \mathcal{Q} and background scattering subspace \mathcal{P} by introduction of the corresponding projection operators Q and P . Using the corresponding decomposition of the scattering Hamiltonian H it is possible to express the matrix elements $\langle \epsilon' | T | \epsilon \rangle = T(\epsilon', \epsilon)$ as sum of the background and resonance terms. We choose

$$Q = |\varphi_d\rangle\langle\varphi_d|, \quad P = \int d\epsilon d\epsilon' |\phi_\epsilon^+\rangle\langle\phi_{\epsilon'}^+|, \quad (9)$$

where $\langle \mathbf{r} | \varphi_d \rangle$ is the square-integrable function (discrete state function) and $|\phi_\epsilon^+\rangle$ is the scattering solution of the operator PHP . We define the discrete state-energy ϵ_d and the discrete state-continuum coupling $V_{d\epsilon}$ by

$$\epsilon_d = \langle \varphi_d | H | \varphi_d \rangle, \quad V_{d\epsilon} = \langle \varphi_d | H | \phi_\epsilon^+ \rangle. \quad (10)$$

Using these quantities and explicit form of the projection operators [Eq. (9)] it is possible to express energy-dependent complex level shift $F(\epsilon) = \Delta(\epsilon) - i\Gamma(\epsilon)/2$:

$$\Gamma(\epsilon) = 2\pi \int d\epsilon' |V_{d\epsilon'}|^2, \quad \Delta(\epsilon) = \frac{1}{2\pi} \mathcal{P} \int d\epsilon' \frac{\Gamma(\epsilon')}{\epsilon - \epsilon'}. \quad (11)$$

The quantities ϵ_d and $V_{d\epsilon}$ fully describe resonant scattering.

The main assumption of the FFR method is the confinement of the discrete state wave function associated with the resonance inside the R -matrix sphere Ω . Then the discrete state can be expressed in terms of the R -matrix basis (2):

$$|\varphi_d\rangle = \sum_{E_k \in \Sigma_{\text{res}}} c_k |\Psi_k\rangle. \quad (12)$$

The region Σ_{res} is chosen so that it covers all the spectral domain where the discrete state interacts with the background continuum. The requirement of vanishing of the discrete state wave function outside the R -matrix sphere gives the condition

$$r_{N+1}^{-1} \langle \bar{\Phi}_\chi | \varphi_d \rangle'_{r_{N+1}=r_\Omega} = \sum_{E_k \in \Sigma_{\text{res}}} c_k w_{\chi k}(r_\Omega) = 0. \quad (13)$$

The corresponding projection operators Q and P can be defined by

$$Q = \sum_{E_j, E_k \in \Sigma_{\text{res}}} |\Psi_j\rangle c_j c_k \langle \Psi_k|, \quad P = 1 - Q. \quad (14)$$

With the background Hamiltonian $H_{\text{bg},\Omega} = PH_\Omega P$ it is possible to solve the background R -matrix problem

$$H_{\Omega,\text{bg}} |\Psi_j^{\text{bg}}\rangle = E_j^{\text{bg}} |\Psi_j^{\text{bg}}\rangle, \quad |\phi_\epsilon\rangle = \sum_j A_{\epsilon j}^{\text{bg}} |\Psi_j^{\text{bg}}\rangle \quad (15)$$

corresponding to Eqs. (3) and (1). Then it is possible to calculate ϵ_d and $V_{d\epsilon}$ using Eq. (10) and Eq. (11) gives energy-dependent width and level shift.

Since condition (13) does not define the discrete state unambiguously, another criterion of the resonance definition is needed. It can be found by comparison with a similar system possessing no resonance in the region Σ_{res} represented by the Hamiltonian H^0 (its restriction to the sphere Ω is denoted H_Ω^0 , and corresponding eigenstates and eigenenergies are denoted by $|\phi_{\chi k}^0\rangle$ and $E_{\chi k}^0$). This model system is usually represented by the target molecule plus noninteracting free electron.

It is possible to show that under certain conditions⁸ the expansion coefficients c_k in Eq. (12) are solutions of the system of linear equations

$$\sum_{E_k \in \Sigma_{\text{res}}} c_k \langle \phi_{\chi j}^0 | \Psi_k \rangle = 0, \quad E_{\chi j}^0 \in \Sigma_{\text{res}}. \quad (16)$$

In realistic cases it is usually impossible to find H^0 such that solution of this system exists. However, it is possible to find an approximation of the overlaps $\langle \phi_{\chi j}^0 | \Psi_k \rangle$ such that condition (13) is satisfied when Eq. (16) is solved:⁸

$$\langle \phi_{\chi j}^0 | \Psi_k \rangle \sim \frac{1}{E_k - E_{\chi j}^0}. \quad (17)$$

TABLE I. Exponents of the continuum basis set.

s	p	d
0.130 137	0.104 354	0.111 252
0.101 981	0.082 488	0.089 412
0.080 524	0.065 610	0.072 361
0.063 367	0.052 121	0.058 496
0.049 648	0.041 110	0.047 005
0.038 298	0.032 122	0.037 397
0.029 151	0.024 635	0.029 225
0.021 901		

III. APPLICATION TO THE FLUORINE MOLECULE

In all the calculations performed the R -matrix sphere Ω of radius $r_\Omega=10$ bohrs has been used. Since the dipole moment of F_2 is zero and its polarizability is small, it is sufficient to consider the scattered electron as free in the outer region and set $V_{ilmi'l'm'} \equiv 0$ in Eq. (7). The target is represented by the CC-pVTZ basis set,²¹ and the continuum basis set used in all the calculations has been taken from the previously published R -matrix calculation¹¹ and is listed in Table I.

Since the continuum basis set has been optimized by fitting the set of spherical Bessel functions to the set of Gaussians^{22,23} for the given angular momentum quantum number, this basis set might not be appropriate for representation of continuum wave functions for higher energies. It is difficult to fit higher Bessel functions with many nodes by the linearly independent Gaussians. Continuum states with considerable contribution of these higher Bessel functions are not represented well by the used continuum Gaussian basis set. The exact solution of the free particle R -matrix problem gives zero phase shift for every energy of the free particle. In order to estimate the energy interval of validity of the Gaussian continuum basis set we solved the free particle R -matrix problem in the Gaussian basis set listed in Table I. The corresponding phase shifts are very small for $E \leq 14$ eV (see Fig. 1). This graph shows that the Gaussian basis set listed in Table I is appropriate in the energy region of interest (0–12 eV).

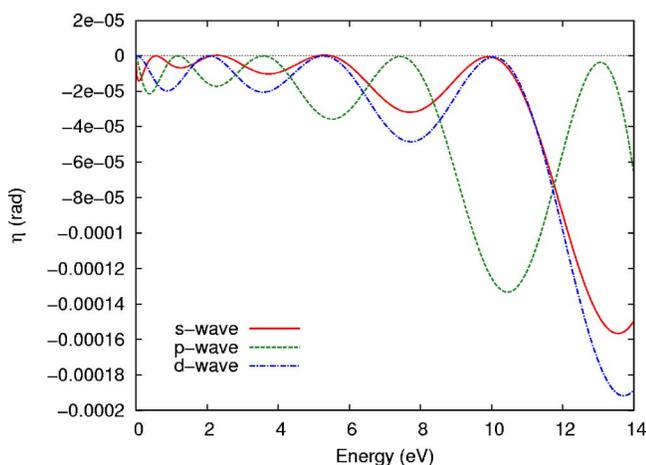


FIG. 1. (Color online) Phase shifts corresponding to potential-free R -matrix problem calculated in the Gaussian continuum basis set described above.

TABLE II. R -matrix poles on the SE level for internuclear separation $R=2.4$ bohrs and configurations strongly contributing to the R -matrix eigenstates with their weights. The energies are relative to the HF ground state. The configurations are represented by the orbital occupied by the scattered electron. Virtual MOs have numbers 1–13 and COs have numbers 14–18.

	E (eV)	Orbital (weight)
1	1.026	14(0.603) 15(0.273)
2	4.730	3(0.520) 15(0.225) 16(0.121)
3	7.880	3(0.446) 4(0.110) 12(0.173) 14(0.105) 15(0.136)
4	15.038	4(0.276) 15(0.120) 16(0.428) 17(0.103)
5	25.677	5(0.447) 17(0.406)
6	31.966	4(0.468) 14(0.104) 15(0.172) 17(0.150)
7	47.722	5(0.177) 17(0.112) 18(0.493)
8	64.700	6(1.0)
9	80.414	5(0.252) 7(0.348) 18(0.154)
10	101.750	7(0.568) 18(0.173)
11	170.494	8(0.959)
12	207.122	9(1.0)
13	239.546	10(0.869)
14	242.274	11(1.0)
15	242.274	12(0.618) 13(0.300)
16	404.273	12(0.120)

In the expansion (2) only the ground electronic state of the target has been included. Due to the ${}^2\Sigma_u$ symmetry the lowest partial wave contributing to the scattering in our basis set is the p wave, and the d wave does not contribute to the scattering. These two facts allow the single channel scattering calculation.

The R -matrix poles E_k as well as transition density matrix used to calculate the R -matrix amplitudes¹⁶ in Eq. (6) have been calculated using the MRCI program package DIESEL.¹⁷ The R -matrix amplitudes as well as elastic scattering eigenphases and cross sections have been calculated using R -matrix program package by Nestmann *et al.*⁶ Calculations at the different levels of correlation have been carried out. Due to technical complications with implementation of the MRCI method it is usually possible to obtain only four lowest R -matrix poles and corresponding amplitudes at the SEP and CI levels in the case of the fluorine molecule. The calculated R -matrix states $|\Psi_k^{\text{SEP}}\rangle$, respectively, $|\Psi_k^{\text{CI}}\rangle$ are

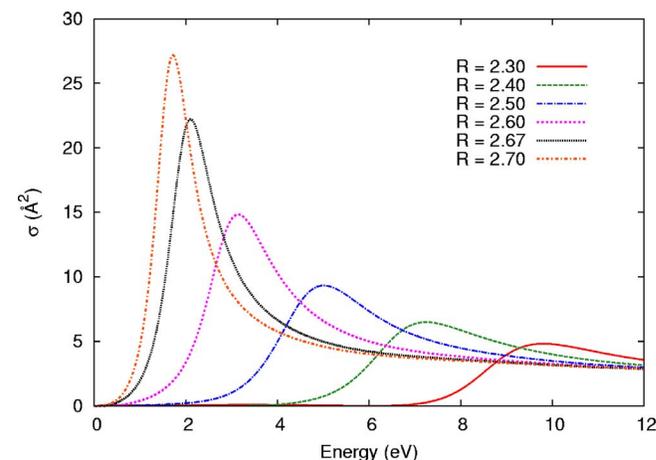


FIG. 2. (Color online) Elastic scattering cross section at the SE level as a function of E at several internuclear separations R (in bohrs).

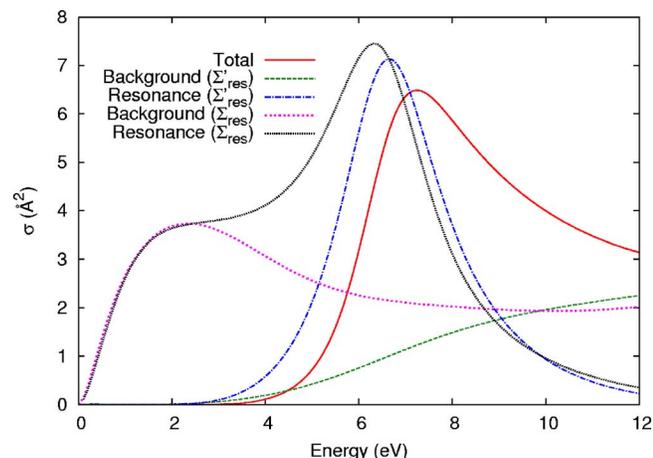


FIG. 3. (Color online) FFR separation of the cross section for internuclear distance $R=2.4$ bohrs in the SE approximation.

completed by the R -matrix states calculated on the SE level $|\Psi_k^{SE}\rangle$ and orthogonalized on $|\Psi_k^{SEP}\rangle$, respectively, $|\Psi_k^{CI}\rangle$ (keeping the original space unchanged) forming a new basis set

$$\begin{pmatrix} \{|\Psi^{CI,SEP}\rangle\} \\ \{|\Psi^{SE'}\rangle\} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ A & B \end{pmatrix} \begin{pmatrix} \{|\Psi^{CI,SEP}\rangle\} \\ \{|\Psi^{SE}\rangle\} \end{pmatrix}. \quad (18)$$

The restricted Hamiltonian $H_{\Omega,N+1}$ is diagonalized in the basis set $\{|\Psi^{SE'}\rangle\}$ and resulting R -matrix poles and amplitudes are added to those calculated on the SEP, respectively, CI level.

The FFR method has been used to calculate the discrete state. The Σ_{res} region has been taken such that it contains the four lowest R -matrix states. The separation of the cross sections and phase shifts to the resonance and background parts has been calculated as well as the discrete state-continuum coupling and the discrete state energies. The data obtained can be therefore used to construct the NRM in the future work. Discussion of nuclear dynamics is, however, beyond the scope of the present paper.

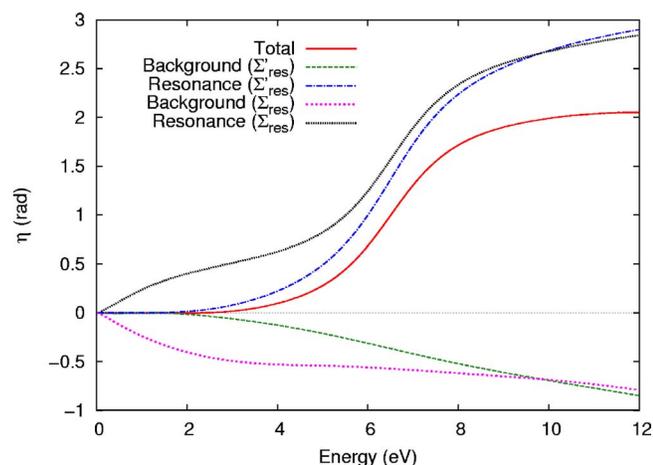


FIG. 4. (Color online) FFR separation of the eigenphase for internuclear distance $R=2.4$ bohrs in the SE approximation.

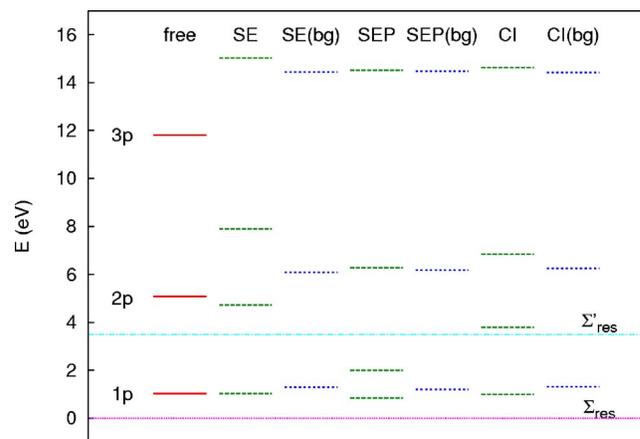


FIG. 5. (Color online) Lowest R -matrix poles of the free particle compared with poles calculated at different levels of correlation and with the corresponding background R -matrix poles. In the case of the SE and SEP poles the energy is relative to the HF energy of the neutral molecule, and in the case of CI poles the energy is relative to the SDCI energy of the neutral target. The regions Σ_{res} and Σ'_{res} are bounded by corresponding lines and the top of the picture.

IV. RESULTS

A. Static exchange (SE) and static exchange with polarization (SEP)

Before the discussion of the SEP calculation we briefly discuss results of the SE calculation. This is important for understanding of the effects of correlation included at the SEP and CI levels. At this level of correlation 16 R -matrix poles have been calculated for every considered internuclear separation R near the equilibrium internuclear distance $R_{eq} = 2.67$ bohrs. Configurations containing the scattered electron in the virtual MOs contribute to the eigenstates of the restricted Hamiltonian with coefficients comparable to configurations containing the scattered electron in the COs (see Table II as an example for $R=2.4$ bohrs). Several higher eigenstates of $H_{\Omega,N+1}$ consist of single configurations with the electron in the virtual MO. Corresponding amplitudes in Eq. (6) are zero, since the MOs vanish on the sphere. These eigenstates do not contribute to the R -matrix (6) at all.

The integral cross section of the electron-F₂ collision for

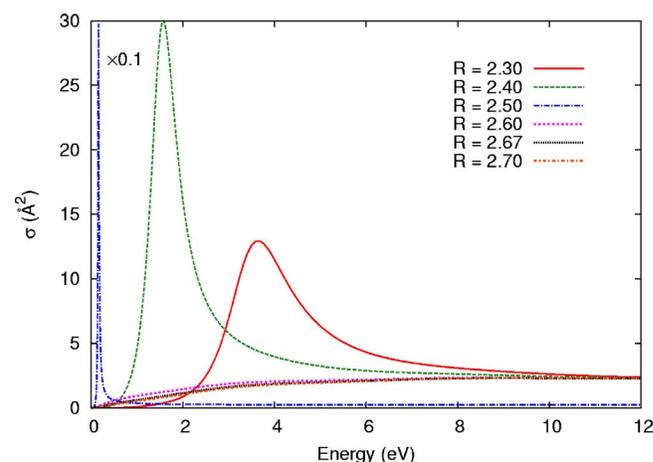


FIG. 6. (Color online) Elastic scattering cross section in the SEP model as a function of E in several internuclear separations R (in bohrs).

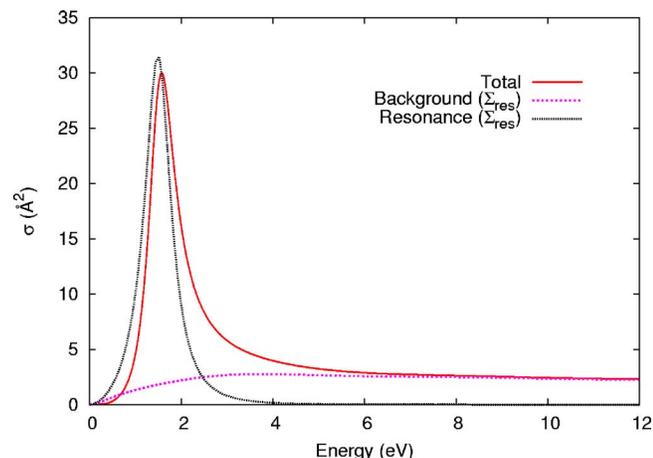


FIG. 7. (Color online) FFR separation of the cross section at the SEP level of correlation for internuclear separation $R=2.4$ bohrs calculated including four lowest R -matrix eigenstates into Σ_{res} .

several internuclear distances is presented in Fig. 2. This figure shows a well pronounced peak located at 2.1 eV with a value of 22.2 \AA^2 for the equilibrium internuclear separation. The resonance structure becomes narrower as R approaches the crossing point of the potential curve of neutral molecule ground state with the negative ion.

The FFR method has been used to separate the discrete state in two variants. In one of them the Σ_{res} region includes the four lowest R -matrix poles in all considered geometries. For small internuclear separations ($R < R_{\text{crit}}$) the contribution of the lowest R -matrix eigenstate $|\Psi_1\rangle$ to the discrete state should be negligible. The approximation¹⁷ of the overlaps, however, leads to unreasonably large value of coefficient c_1 . The separation by projectors Q and P results therefore into an additional peak in the background cross section. The corresponding separations of the cross section and eigenphases are shown in Figs. 3 and 4 for $R=2.4$ bohrs. In order to avoid this behavior another calculation has been carried out with Σ'_{res} excluding the lowest R -matrix eigenstate (see Fig. 5). The corresponding cross section and eigenphase separation are also plotted in Figs. 3 and 4.

With increasing R ($R > R_{\text{crit}}$) it is necessary to include the lowest R -matrix state into Σ_{res} in order to avoid the poles with small imaginary part in the background T matrix and to obtain smooth transition to the bound state region of R .

Results of the R -matrix calculations at the SE level of correlation show the resonance structure in every considered geometry (the presence of the resonance in the equilibrium internuclear separation is in agreement with earlier results of Morgan and Noble¹⁵).

TABLE III. R -matrix poles on the SEP level for internuclear separation $R=2.4$ bohrs and configurations strongly contributing to the R -matrix eigenstates with their weights. The representation of the configurations is the same as in Table II.

	E (eV)	Orbital (weight)
1	0.848	3(0.222) 14(0.517) 15(0.185)
2	1.999	3(0.678) 15(0.145)
3	6.266	4(0.229) 14(0.217) 15(0.278) 16(0.209)
4	14.509	4(0.271) 16(0.443) 17(0.103)

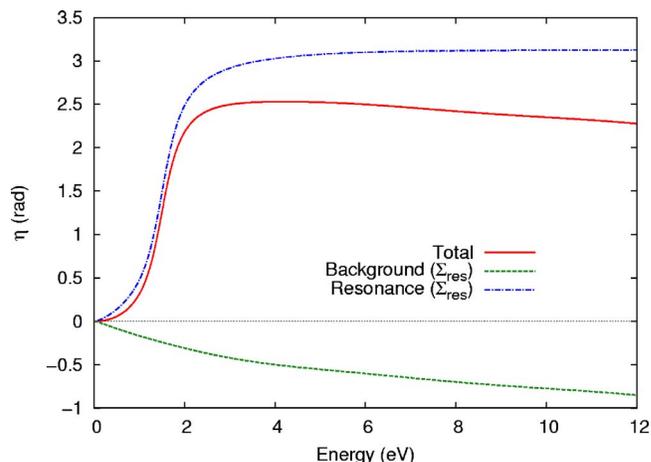


FIG. 8. (Color online) FFR separation of the eigenphases at the SEP level of correlation for internuclear separation $R=2.4$ bohrs calculated including four lowest R -matrix eigenstates into Σ_{res} .

At the SEP level of correlation 4 R -matrix poles have been calculated and additional 16 poles have been added on the SE level. Single excitations of the neutral molecule contribute to the SEP R -matrix poles. As at the SE level, configurations consisting of the molecule in the HF ground state and the scattered electron in the virtual MO or CO still represent the major contribution to the CI expansion of the $H_{\Omega, N+1}$ eigenstates. However, the presence of single excitations of the neutral molecule strongly affects the respective weights of these dominating configurations (compare Tables II and III). The calculated cross sections for several values of R are presented in Fig. 6. Contrary to the SE calculation, for three largest considered geometries, the ionic state is bound. This means that at the SEP level of correlation the crossing point of the neutral target ground state potential with the first R -matrix pole curve is shifted towards smaller values of R compared to the SE level. The presence of the bound ionic state in the equilibrium geometry is in agreement with results of Morgan and Noble.¹⁵

The results of the FFR separation are shown in Figs. 7 and 8. The discussion of the lowest R -matrix pole exclusion from Σ_{res} remains valid also in the SEP calculation, but the

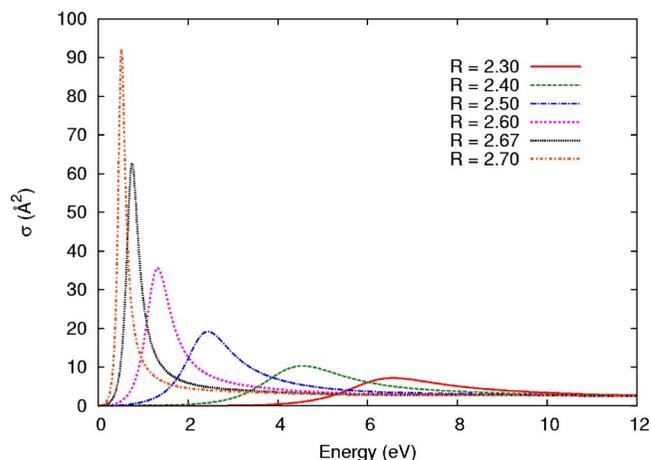


FIG. 9. (Color online) Elastic scattering cross sections for several internuclear separations R (in bohrs) calculated at the CI level.

TABLE IV. R -matrix poles at the CI level for internuclear separation $R = 2.4$ bohrs and the configurations strongly contributing to the R -matrix eigenstates with their weights. The representation of the configurations is the same as in Table II. The energies are relative to the SDCI energy of the neutral target.

	E (eV)	Orbital (weight)
1	0.988	14(0.551) 15(0.236)
2	3.789	3(0.686) 15(0.138)
3	6.848	3(0.163) 4(0.181) 14(0.190) 15(0.182) 16(0.162)
4	14.640	4(0.255) 16(0.403)

critical geometry R_{crit} , where the lowest R -matrix pole becomes important, is smaller than in the SE calculation. Calculated R -matrix poles show good agreement with previously published SEP work enabling us to compare our calculations at the CI level with previous R -matrix results.¹¹ The small discrepancies are caused by different compact basis sets used.

B. Configuration interaction (CI)

At the CI level of the theory four R -matrix poles have been calculated for a range of geometries from 2.0 to 5.5 bohrs. These CI poles have been completed by 16 SE poles. For comparison with calculations at different levels of correlation the R -matrix poles and configurations dominating in corresponding eigenstates are listed in Table IV (compare with Tables II and III). These eigenstates consist of configurations with scattered electron in the continuum as well as of configurations with scattered electron in virtual MOs, both types with comparable weights. The comparison of numbers of configuration state functions (CSFs) in the SEP and CI calculations is presented in Table V.

The calculated cross sections are plotted in Fig. 9. This figure shows resonance structure at every considered internuclear distance with lower energies and smaller widths than in the SE calculation. The corresponding peak in the cross section is located at 0.75 eV for the equilibrium internuclear separation. With increasing internuclear distance the contribution of the excited configuration increases in the target eigenstates as well as in the eigenstates of $H_{\Omega, N+1}$ ($3\sigma_g \rightarrow 3\sigma_u$ since these orbitals become degenerated asymptotically). These excitations have not been allowed in the previous models of correlation. Double excitations allow the energy of the target state as well as the energies of the poles to be lower than in the previous models and more consistent with previous calculations of the neutral target ground state potential curves.²⁵ The electron affinity calculated at this level of correlation (2.2 eV) is much closer to the experimental value²⁶ (3.4 eV) than the value obtained at the SEP

TABLE V. Counts of CSFs generated in the SEP and CI calculations by allowed excitations from the given reference set for internuclear distance $R = 2.4$ bohrs.

	SEP	CI
Target	0	64154
Ion	1430	612582

TABLE VI. Locations of the crossing points (bohr) where the resonance turns into the bound state.

Morgan and Noble (Ref. 15)	Ingr <i>et al.</i> (Ref. 4)	Brems <i>et al.</i> (Ref. 11)	This work
2.56	2.62	2.41	2.76

level¹¹ (13.5 eV). The discrepancy of our results with the experimental value is caused by the correlation imbalance in the calculation of the neutral target state and the negative ion state as well as not sufficiently large R used for calculation of the electron affinity. The incorrect value obtained at the SEP level is understandable, because the absence of double excited configurations in the wave functions leads to incorrect behavior of the potential curves for large values of R . In the SEP calculation the target ground state is represented by single closed-shell Slater determinant. In the asymptotic region of internuclear separations this gives ground state of system $F^+ + F^-$ and does not take into account the contribution of the open-shell configurations. Therefore the CI level of calculation improves the description of the target considerably for large internuclear distances.

The R -matrix pole curves as functions of the internuclear distance are plotted in Fig. 10. These curves show the avoided crossing near the crossing point of the neutral target state with the lowest R -matrix pole. The crossing point where the resonance turns into the bound state is located at $R_{\text{thr}} = 2.76$ bohrs at variance with previously calculated results^{4,11,15} (see Table VI). The determination of the crossing point, which is of particular importance in the nuclear dynamics calculations, is complicated by the unbalanced correlation in independent calculations of the ionic and neutral target states.

The FFR method has been again used to determine the discrete state and corresponding separation of the cross sections and eigenphases for internuclear distance $R = 2.4$ bohrs (see Figs. 11 and 12). Again two calculations

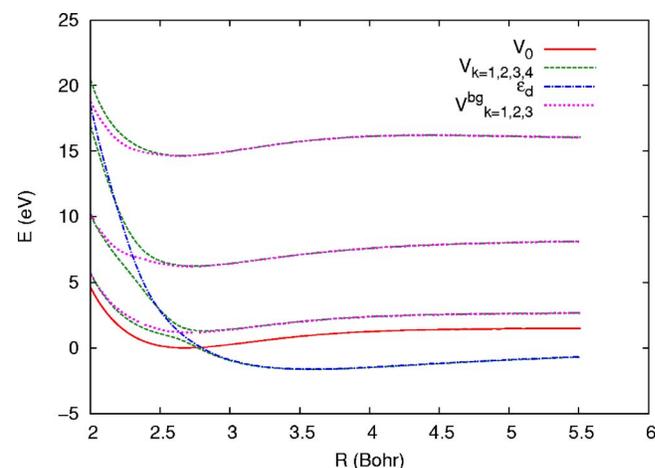


FIG. 10. (Color online) R -matrix poles calculated at the CI level as function of the internuclear distance. V_0 is the potential curve of the neutral target, $V_{k=1,\dots,4}$ are the R -matrix pole curves, $V_{k=1,\dots,3}^{\text{bg}}$ are the background R -matrix pole curves, and ϵ_d is the energy of the discrete state wave function. All energies are relative with respect to the neutral target energy in the equilibrium internuclear distance.

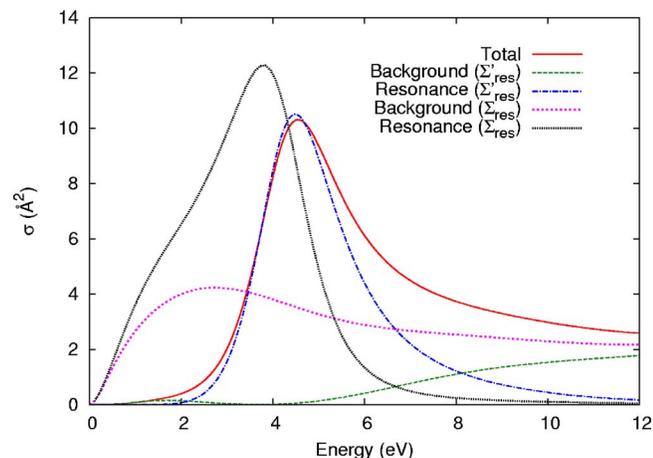


FIG. 11. (Color online) FFR separation of the cross section at the CI level of correlation for internuclear separation $R=2.4$ bohrs.

have been carried out in order to study the effect of inclusion of the lowest pole into the region Σ_{res} (see Fig. 5). The internuclear distance, where the lowest R -matrix pole becomes important, is near the avoided crossing point of the first and the second R -matrix state.

In order to compare the resonance positions in the considered correlation models the poles ϵ_{res} of the T matrix have been estimated assuming that the imaginary part is small enough to allow the solution in the form

$$\Re \epsilon_{\text{res}} - \epsilon_d - \Delta(\Re \epsilon_{\text{res}}) = 0, \quad \Im \epsilon_{\text{res}} = \frac{1}{2}\Gamma(\Re \epsilon_{\text{res}}). \quad (19)$$

Comparison of these estimated resonance positions is presented in Fig. 13. This figure shows that the resonance energies calculated at the CI level are larger than the values calculated at the SEP level and smaller than those calculated at the SE level.

V. CONCLUDING REMARKS

The Bonn implementation¹⁶ of the R -matrix method has been used to study the ${}^2\Sigma_u$ resonance in electron scattering off the fluorine molecule using different levels of correlation including recently implemented SD-MRCI approach. The

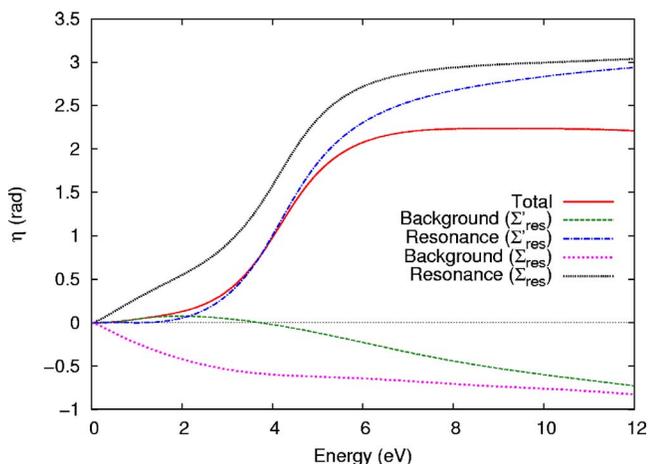


FIG. 12. (Color online) FFR separation of the eigenphases at the CI level of correlation for internuclear separation $R=2.4$ bohrs.

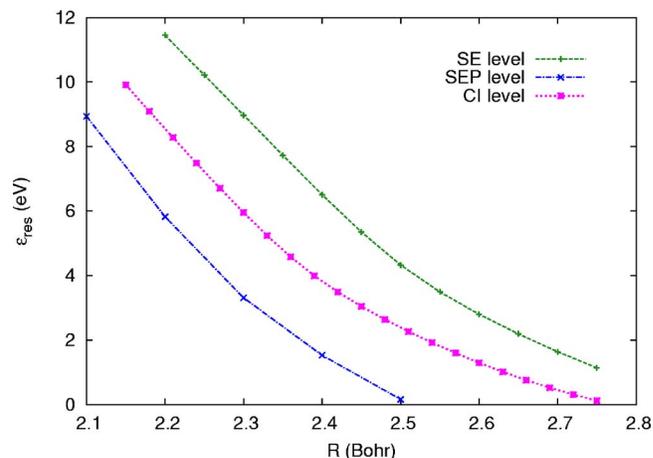


FIG. 13. (Color online) Approximate resonance position at different levels of correlation.

cross section calculated at the SE level of correlation shows well pronounced resonance for the equilibrium internuclear distance, while the SEP calculation yields a bound ionic state in this geometry. The obtained results are in agreement with previously published works of Morgan and Noble.¹⁵ The resonance structure appears again at the CI level, but with different energy and width. The FFR method has been used to separate the resonance and to determine its coupling with the background continuum at three levels of correlation. The effect of the correlation on the resonance position and width has been studied. We have shown that inclusion of the doubly excited configurations in SD-MRCI expansions of the wave functions improves the results of the scattering calculations for larger internuclear distances, since the SD-MRCI approach correctly includes the neutral fragmentation channels of the target molecule. Our results show how the position of the crossing point of the neutral target potential curve with the ionic potential curve depends on the included correlation. Unlike previous results our calculation shows that the ion is unstable towards autodetachment even at the equilibrium internuclear separation of the neutral molecule. The results obtained here from the CI calculation present the first step in the construction of the nonlocal resonance model of the nuclear dynamics which will show the correlation effects in the DEA and VE of the fluorine molecule. This will be a subject of the forthcoming work.

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