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Commentationes

Calculations of Potential Energy Surfaces in the Complex Plane

V. The $^2\Sigma^+$ and $^2\Pi$ States of HF^+

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We calculate the energies of the $^2\Sigma^+$ and $^2\Pi$ states of the HF^+ system by the *ab initio* restricted Hartree-Fock method at a number of real and complex values of the internuclear separation. The energies of the associated spin-orbit states are calculated via a semiempirical scheme. The complex intersection point of these energy curves, an integral component of a semiclassical theory of electronic transitions, is determined by the *ab initio* calculations. The intersection point is also determined, for comparative purposes, by other methods of analytic continuation, i.e., Gaussian and rational-fraction fits to the real-valued energy calculations. Semiclassical dynamical calculations of the cross section for the process $F(^2P_{3/2})+H^+ \rightarrow F(^2P_{1/2})+H^+$ using the various intersection points yield differences up to 20%.

Key words: Energy surfaces in the complex plane – HF^+ – Semiclassical collision theory – Spin-orbit interaction

1. Introduction

Recent semiclassical calculations involving complex-valued classical trajectories have been carried out for electronic transitions in the $H^+ + H_2$ [1], $H^+ + D_2$ [2–4], $X + H_2$ ($X \equiv$ halogen) [5, 6], $F + H^+$ [7] and $F + Xe$ [7] collision systems. The calculations on $F + H^+$ and $F + Xe$ are based on the Stueckelberg [8] model of electronic transitions, and those on the triatomic systems employ a semiclassical theory [9, 10] which is essentially a generalization of the Stueckelberg model to systems involving internal as well as translational nuclear degrees of freedom. Within this framework the internal nuclear degrees of freedom have been treated both semiclassically [1–5] and quantum mechanically [6]. In the latter case, where only the translational degree of freedom is treated semiclassically, the problem is reduced to the Stueckelberg model where the transitions are between vibronic states. In all these calculations, a two-state approximation is imposed, and we consider pairs of adiabatic potential energy surfaces (or curves) which do not intersect for real values of nuclear coordinates. If these surfaces are

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analytically continued into the complex plane, intersection points are found. For a two-state problem, the adiabatic surfaces are found as eigenvalues of a two-by-two matrix and can be expressed as $A \pm \sqrt{B}$, where A and B are single-valued functions of the nuclear coordinates. Hence, one can consider the potential as a single analytic function in complex space having two Riemann sheets corresponding to the two branches of the square root function. The intersections of the adiabatic surfaces are equivalent to the branch points of this analytic potential energy function [11–15]. Quantum transitions are effected by complex-valued classical trajectories propagating on the surfaces and switching surfaces continuously (i.e., with no discontinuities in any component of the nuclear position or momenta) at the branch points. The local probability of such a transition is $\exp(-2\mathrm{Im}\phi/\hbar)$, where ϕ is the action accumulated in propagating around the branch point. Hence, the transition probability is strongly dependent upon the position of the branch points and the value of the potential in their neighborhood.

The accuracy of these dynamical calculations depends upon the accuracy of the analytic continuation of the surfaces to their intersection points. Therefore, we have initiated studies of various methods of analytic continuation. The most rigorous method involves the *ab initio* calculation of the potentials at complex values of the nuclear coordinates. For the H_3^+ [14] and FH_2 [15] systems we have carried out *ab initio* LCAO-MO calculations in complex nuclear coordinate space to locate some of the intersection points between various surfaces. The classical dynamical calculations on these triatomic systems involve the solution of the coupled classical equations of motion. The propagation to the complex intersection point requires imaginary steps, and since the nuclear degrees of freedom are coupled, both the translational and internal nuclear coordinates become complex. Each of these yields a complex contribution to the phase, and it is difficult to isolate specific effects of any inaccuracies in the analytic continuation of the potential surfaces. However, for a diatomic system there is a single nuclear coordinate, and the effect of any inaccuracy in the analytic continuation will be apparent. Hence in the present work we focus on the analytic continuation of the potential energy curves in a diatomic system, namely HF^+.

There have been recent quantum mechanical [16] and semiclassical [7] studies of the process

$$F(^2P_{3/2}) + H^+ \rightarrow F(^2P_{1/2}) + H^+, \tag{1}$$

which involves a transition from the ground to the first excited spin-orbit state of the fluorine atom. Both studies used the same potential energy curves, obtained from near-Hartree-Fock limit calculations (without spin-orbit interaction) by Julienne, Krauss and Wahl [17]. The ground state ($^2\Pi$) potential curve has a minimum of -0.129 hartree at an internuclear separation of $r = 1.8$ bohr, and the first excited state ($^2\Sigma^+$) curve has a minimum of -0.012 hartree at $r = 2.25$ bohr and a maximum of 0.0027 hartree at 4.0 bohr (the energies are related to separated $F + H^+$). Although the curves do not intersect on the real axis, they have a common asymptote. When the spin-orbit interaction is considered, the curves are split asymptotically by 0.00184 hartree, the energy separation between the $^2P_{3/2}$ and $^2P_{1/2}$ states of the fluorine atom.

The semiclassical studies of Preston, Sloane and Miller [7] involved the analytic continuation of the potential curves to their intersection points in the complex nuclear coordinate plane. To find these points, they fit the difference between the $^2\Pi$ and $^2\Sigma^+$ curves on the real axis to a Gaussian form which was then analytically continued. Although the semiclassical results are in fairly good agreement with the quantum results, there are small discrepancies which might be reduced through a more accurate analytic continuation of the curves.

It is the purpose of this paper to investigate various methods of analytic continuation of the potential curves of the HF$^+$ system. In Section 2 we describe the results of the *ab initio* restricted Hartree-Fock calculations of these curves for both real and complex values of r. Including spin-orbit interaction as a perturbation in the manner of Julienne *et al.* [17], we then locate a complex intersection point, which represents the most accurate intersection point of the spin-orbit states within the framework of the restricted Hartree-Fock approximation. In Section 3 we locate complex intersection points by various techniques of curve-fitting to the *ab initio* results. These techniques include rational fractions and the Gaussian form used by Preston *et al.* [7]. The results of these techniques of analytic continuation are discussed and compared with respect to their possible influence on dynamical calculations.

2. *Ab initio* Calculations

The diatomic molecular ion radical HF$^+$ can be considered as a fluorine atom interacting with a proton. In the ground state the π molecular orbitals are partially filled, resulting in $^2\Pi$ symmetry, and the first excited state $^2\Sigma^+$ has a single occupied σ molecular orbital. Since these states are of different symmetries, they do not interact under the nonrelativistic Hamiltonian. As mentioned in the Introduction, they have a common asymptotic energy at infinite H$^+$–F separation. However, when spin-orbit interaction is included, the $^2\Pi$ and $^2\Sigma^+$ states do mix, resulting in an asymptotic splitting of $\lambda = 0.00184$ hartree. An *ab initio* calculation of the spin-orbit interaction energy is extremely difficult and has only been attempted for a small number of molecular systems [18–21]. However, semiempirical estimates of the spin-orbit interaction based on the atomic term values are often reasonably accurate[1]. In this (perturbation) scheme the off-diagonal electronic matrix element connecting the two interacting states is a constant equal to $-\sqrt{2}\lambda/3$. The resulting two-by-two Hamiltonian matrix is given as [7, 17]

$$\boldsymbol{H} = \begin{Bmatrix} V_\Pi + \lambda/3 & -\sqrt{2}\lambda/3 \\ -\sqrt{2}\lambda/3 & V_\Sigma \end{Bmatrix}, \tag{2}$$

where V_Σ and V_Π are the energies of the $^2\Sigma^+$ and $^2\Pi$ states (in the absence of spin-orbit interaction). Diagonalizing $\boldsymbol{H}$ we obtain the two energies

$$E_\pm = \{V_\Sigma + V_\Pi + \lambda/3 \pm [(V_\Pi - V_\Sigma + \lambda/3)^2 + 8\lambda^2/9]^{1/2}\}/2, \tag{3}$$

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[1] The dominant term in the spin-orbit Hamiltonian is the one-center $l.s$ interaction (atomic value). Two-center terms represent enhanced shielding and tend to slightly reduce the magnitude of the interaction.

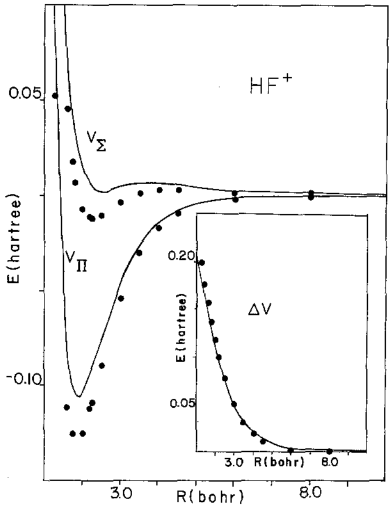

Fig. 1. *Ab initio* potential curves for the HF$^+$ system. The solid lines represent the present calculation, and the solid circles denote the results of Julienne *et al.* [17]. The curves are shown relative to their asymptotic degenerate value, which differs for the two calculations. In the insert we depict the difference $\Delta V = V_\Sigma - V_\Pi$ versus internuclear separation. Again, the solid curve represents our results, and the dots the results of Ref. 17

where $E_-(E_+)$ is the new ground (first excited) state energy. The energy difference is simply

$$\Delta E(r) = [(V_\Pi(r) - V_\Sigma(r) + \lambda/3)^2 + 8\lambda^2/9]^{1/2}. \qquad (4)$$

For nonzero values of λ, there are no real-valued solutions to $\Delta E(r) = 0$, and the potentials do not intersect. However, if the potentials are analytically continued to complex values of r, one can, at least in principle, find a value $r = r_c$ for which $\Delta E = 0$. r_c is then a complex intersection point of the surfaces i.e., a branch point of the potential function.

We have performed generalized restricted Hartree-Fock (GRHF) calculations of V_Σ and V_Π at several real and complex values of r. E_+ and E_- were found through Eq.(3) and are called GRHF+SO energies. The GRHF calculations employed the method of Chang, Davidson and Vincow [22] as modified and programmed by Iwata and Morokuma [23]. Further modifications of Iwata and Morokuma's program were made to permit the calculation of electronic energies for molecules at complex nuclear geometries[2].

A contracted Gaussian-type-orbital (GTO) basis set was used for all of the calculations. This basis set consisted of ten s and six p functions on the fluorine atom, contracted to five s and three sets of p orbitals, and five s functions for the hydrogen atom contracted to three s functions. The exponents and coefficients for the seventeen contracted functions are those of Dunning [24].

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[2] The techniques involved in complex-valued *ab initio* MO calculations are discussed in Refs. 11, 14 and 15.

The $^2\Sigma^+$ and $^2\Pi$ GRHF potential curves (V_Σ and V_Π) are represented for real values of r by the curve in Fig. 1[3] along with the results of Julienne, Krauss and Wahl [17] which are denoted by the solid circles. The latter employed a large Slater-type-orbital (STO) basis which resulted in a lower energy for separated atoms (by 0.004627 hartree) and stronger bond energies for both electronic states. In fact, in our calculation the minimum in V_Σ is higher in energy than the separated atoms. However, the energy difference ΔV between these states is nearly identical for the two calculations, as shown in the insert in Fig. 1. Since the location of the intersection point in the two-by-two GRHF+SO secular equation depends only upon ΔV and λ, the larger differences between the two calculations are not expected to be important in locating the complex intersection points. However, these differences will be reflected in the value of the energies in the neighborhood of the intersection points.

Rational-fraction techniques [12, 13, 25] were used to facilitate the *ab initio* search for the intersection points. A rational-fraction constructed solely from real-valued data of six to eight figure accuracy is expected to represent the energy difference to six figures when analytically continued no further than $\mathrm{Im}\,r = 0.5$ bohr [13]. Since Preston *et al.* [7] estimated the complex intersection point closest to the real axis to have an imaginary part greater than 2.5 bohr, we initially carried out complex-valued GRHF+SO calculations at five different complex values of r[4]. The values of $(\Delta E(r))^2$ for these five points along with the fifteen real-valued GRHF+SO calculations in the range $r = 1$ to 10 bohr were fit to a rational-fraction[5]. [The rational-fraction must reproduce the branch-point structure implicit in the *ab initio* potential energy function, which is exhibited by a square root function (see Eq.(4)). This "square root character" was incorporated into the rational-fraction by squaring the input values, i.e. $(\Delta E(r))^2$, and then taking the square root of the rational fraction.] The first estimate of the intersection point was obtained by setting the rational-fraction to zero and solving for a complex root r_{c_1}. A complex-valued GRHF+SO calculation was then performed at that point, and the resulting $(\Delta E(r))^2$ was included in the data for a second rational-fraction[5]. This new rational-fraction was used to obtain a second estimate r_{c_2}, and this iterative procedure was continued until $|\Delta E(r_{c_4})| < 10^{-5}$ in the GRHF+SO calculations, where r_{c_4} is the intersection point $r_c = 7.49426 \pm 3.00887i$ bohr.

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[3] Actual calculations were carried out at $r = 1.0$, 1.25, 1.50, 1.75, 2.00, 2.25, 2.50, 2.75, 3.00, 3.25, 3.50, 3.75, 4.00, 4.25, 4.50, 4.75, 5.00, 5.25, 5.50, 6.00, 6.50, 7.00, 7.50, 8.00, 8.50, 9.00, 9.50, 10.0 and ∞ bohr, and the results are available upon request to one of the authors (KM).

[4] Calculations were initially carried out for $r = 5+0.3i$, $7.0+0.3i$, $7.0+1.0i$, $7.0+2.0i$, $8.0+0.3i$ bohr. Later the potentials were evaluated at $4.39273+2.45435i$, $7.5974+3.09301i$, $7.50333+2.9919i$, and $7.49476+\alpha 3.00887i$ bohr, were $\alpha = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1$.

[5] In previous work (see Ref. 14) only $\Delta E(r_{c_1})$ was included in the input data for the next rational-fraction. However, the *ab initio* energies (and energy differences) are real functions of complex r and thus satisfy the Schwarz Reflection Principle (see Ref. [26]. A rational-fraction constructed from real input is a real function of the complex variable r, but when complex-valued input data are used, this is no longer the case. However, using both $\Delta E(r_{c_1})$ and $\Delta E(r_{c_1}^*)$ as input creates localized reflection symmetry in the region near r_{c_1}. This increases the range of convergence of the analytically continued rational-fraction to larger values of $\mathrm{Im}\,r$.

3. Curvefitting Techniques

In order to find the location of the complex intersection point from the real-valued potential curves of Julienne *et al.* [17], Preston *et al.* [7] fit the energy difference $\Delta V = V_\Sigma - V_\Pi$ to a Gaussian,

$$\Delta V = A \exp(-Br + Cr^2), \tag{5}$$

and solved for the value of r which satisfies $\Delta E = 0$ (see Eq.4). In this manner the intersection point may be written analytically as

$$r_c = [B \pm (B^2 - 4C[\ln(A/\lambda) \pm i \cos^{-1}(1/3)])^{1/2}]/2C. \tag{6}$$

Applying this procedure to our real-valued *ab initio* potential curves, and obtaining the parameters A, B, C with a generalized non-linear least squares fit[6], we found that the value of r_c was sensitive to the particular set of input points which were used, and furthermore did not converge to a limiting value. We used a set of real-valued input points, spaced evenly 0.5 bohr apart. Initially we considered input points in the range $r = 8.5$ to 10.0 bohr which yielded an intersection point of $7.6271 \pm 3.1952i$ bohr. As we increased the number of points the resultant intersection point varied smoothly without converging. By comparison to the *ab initio* result, a "best" Gaussian intersection point, ($7.5795 \pm 2.9795i$ bohr), was found by fitting from 6.0 to 10.0 bohr. Unfortunately, there was no criterion for choosing this particular set of input points.

Another method of analytic continuation is through rational-fractions [25]. In the complex plane the intersection points are found by a simple search for the roots of $\Delta E(r) = 0$. For these studies, we used up to twenty-eight real and nine complex-valued *ab initio* input points. We originally used input points from the range $r = 4.0$ to 10.0 bohr which yielded an intersection point of $7.4300 \pm 3.2041i$ bohr. The inclusion of more input points in the range 1.0 to 3.0 bohr shifted this only to $7.4348 \pm 3.1888i$, which we consider as the converged limit. This method exhibits much more stability than the Gaussian procedure. The addition of a single complex-valued input point did not alter the intersection point very much, but the inclusion of all complex points yielded $r_c = 7.49426 \pm 3.00887i$ bohr.

We compared the effect of these different fits in a simple dynamical calculation on the FH^+ system. The S-matrix elements were constructed from one dimensional phase integrals of the form $\int [2\mu(E - E_\pm - [l + 1/2]^2/2\mu r^2)]^{1/2} dr$ which were evaluated on each energy curve from the classical turning point to r_0 (the real part of r_c), and from r_0 in complex space to r_c. These integrals were evaluated by a convergent Simpson's rule routine in which the quadrature points were provided by a rational-fraction fit of some selected set of input points. For the integrals along the real axis, the entire set of real points was used as input, and either E_+ and E_- or $(\Delta E)^2$ and E_{avg} were the functions analytically continued. For the real-axis integrations, these two methods agreed to four significant figures. The integrals to the complex intersection point were handled in a variety of ways. We calculated the GRHF+SO potential curves at three additional complex points,

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[6] The computer program GENNY was used, courtesy of Professor L. Friedrich, the University of Rochester.

Table 1. Results of the dynamic calculations

r_c (bohr)	fitting procedure for complex integrals	σ	$\lvert S(0)\rvert^2$	$\lvert S(10)\rvert^2$	C[a]
exact[b]	exact[c]	0.00629	0.00033	0.00018	4.1610
exact[b]	E_+, E_-	0.00542	0.00030	0.00015	4.2337
exact[b]	$(\Delta E)^2$, E_{avg}	0.00557	0.00030	0.00016	4.2211
$7.5795 \pm 2.9795i$	$(\Delta E)^2$, E_{avg}	0.00619	0.00032	0.00017	4.1917
$7.4348 \pm 3.1888i$	$(\Delta E)^2$, E_{avg}	0.00502	0.00030	0.00014	4.2816

[a] C is the imaginary part of the phase which is accumulated in propagating in complex space to the intersection point on the initial surface and returning to the real axis on the final surface.

[b] $7.49426 \pm 3.00887i$.

[c] *Ab initio* points at $7.49426 \pm \alpha 3.00887i$, $\alpha = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}, 1$, were used as input for a rational fraction to evaluate the phase integrals in complex space. All other fitting procedures used only real input points.

spaced evenly between r_0 and r_c. The energies at these points as well as at r_0 and r_c provided input to a rational-fraction which was used to evaluate the complex integrals. This procedure is referred to as the "exact" semiclassical method. We also used fits of only the real-valued input points and continued either E_+ and E_- or $(\Delta E)^2$ and E_{avg} to the *ab initio* intersection point, and these results were compared to each other and the exact result. The latter method was also used to evaluate the complex phase integrals to the intersection points determined by the Gaussian and rational-fraction fits. Employing Eqs.(2.7)–(2.14) of Ref. 6 with the phase factor $\delta = +\pi/4$, the phase integrals were used to construct the S-matrix elements, $S(l)$, for each partial wave l, for Reaction (1). The cross section can be written

$$\sigma = \frac{\pi}{2\mu(E+\lambda/3)} \sum_{l=0} (2l+1)\lvert S(l)\rvert^2, \tag{7}$$

where E is the energy in hartree, measured from the common asymptote of V_Σ and V_Π, and μ is the reduced mass of the F+H$^+$ system. The cross sections were evaluated at $E = 0.002$ hartree, and the sum over the partial waves was terminated at $l = 15$, where the turning point on the upper surface is greater than 10.0 bohr. The cutoff in the partial wave summation was applied consistently in all cases.

The results of these calculations are presented in Table 1. The first column lists the intersection point which was used in the calculation, and the second column indicates the functional forms used as input to generate quadrature points for the complex phase integrations. In this column, "exact" refers to the use of the five complex-valued calculations between r_0 and r_c as input to a rational-fraction. The other rational-fractions used only real input. The third column lists the cross sections, and the next two columns list the squares of the S-matrix elements for specific partial waves, namely $l = 0$ and 10. Finally, we compare the imaginary contribution to the phase from the integrals to and from the complex intersection point on the initial and final potential curves respectively. This quantity, labelled C, was calculated for the zeroth partial wave.

Several things are clear from the Table. The analytic continuation of the functions $(\Delta E)^2$ and E_{avg}, which preserves the branch point structure of the potential energy function, is more accurate than the continuation of the functions E_+ and E_-. Furthermore, more error is incurred by the misplacement of the intersection point than by the use of the rational-fraction to generate quadrature points for the integration. Thus if one were to determine an *ab initio* intersection point for a pair of surfaces there is no need to calculate a large number of additional complex-valued input points for the integrations, as these will not greatly improve the accuracy of the calculation.

4. Summary

We have calculated the energies of the $^2\Sigma^+$ and $^2\Pi$ states of the HF^+ system at a variety of real and complex values of the internuclear separation. Aided by a rational-fraction fit, an *ab initio* intersection point for the associated spin-orbit states was found at $r = 7.49426 \pm 3.00887i$ bohr. A rational-fraction fit based entirely on real input points yielded an intersection point of $r = 7.4348 \pm 3.1888i$ bohr and was stable as we varied the number of input points. Cross sections calculated for the electronic transition in the FH^+ system showed a strong dependence on the position of the intersection point. However, the use of an analytic fit by rational-fraction techniques to a set of real input points introduced only a small error in the cross section.

Finally, although the cross section for the intersection point determined by the Gaussian fit is in good agreement with the exact semiclassical results, this intersection point was chosen from a range of possible values. The intersection points determined by different sets of input points did not converge to a limit as more points were added, unlike the rational-fraction method. Without prior knowledge of the *ab initio* intersection point, the Gaussian fitting procedure would have been of little use.

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