J. Phys. Chem. A **2004,** *108,* 8731−8742

Long-Range Interaction in Some Simple Open-Shell Systems, Including Rare-Gas Sulfides: Features of Post-Adiabatic Potentials and Couplings[†]

Mikhail B. Sevryuk* and Lev Yu. Rusin*

Institute of Energy Problems of Chemical Physics, The Russia Academy of Sciences, Leninskiĭ prospect 38, Building 2, Moscow 119334, Russia

Simonetta Cavalli and Vincenzo Aquilanti

Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, I-06123 Perugia, Italy

Received: February 4, 2004; In Final Form: March 30, 2004

The first-order post-adiabatic representations in the sense of Klar and Fano (Klar, H.; Fano, U. *Phys. Rev. Lett.* **1976**, *37*, 1132−1134) are obtained for two-channel stationary Schrödinger equations describing the interaction of the fluorine and chlorine (in the ^{2}P state) and oxygen and sulfur (in the ^{3}P state) atoms with a number of closed-shell particles, in particular, with rare gases, hydrogen, deuterium, and methane. Information on the adiabatic potentials and the nonadiabatic coupling comes mostly from scattering experiments, although some input from ab initio quantum mechanical calculations is also exploited. Various trends in the behavior of the first-order post-adiabatic coupling are analyzed, and the optimal ways to estimate the smallness of this coupling are discussed. The best measure of the strength of the post-adiabatic coupling of order s is found to be the differences between the respective post-adiabatic potentials of orders s and $s + 1$. A rigorous proof is given of the fact that post-adiabatic representations exist only in the important case of a single "slow" degree of freedom.

I. Introduction

A universal tool used to study microscopic properties of matter is provided by the Schrödinger equation. One of the key and frequently used points in the practical implementation of this tool is the separation of all of the degrees of freedom (generalized coordinates) in the system in question into "fast" and "slow" degrees of freedom, depending, for example, on the relative strength of quantum effects or the presence of a small parameter in the problem. The motion associated with the fast coordinates can then be examined at the fixed values of the slow coordinates, and the evolution equations for the slow degrees of freedom are obtained from the initial Schrödinger equation for the whole system by averaging over the fast variables. The prototypical example is the classic Born−Oppenheimer separation[1] of slow nuclear motions from fast electronic degrees of freedom in atomic and molecular systems. This operation takes into account the smallness of the electron mass as compared to the averaged mass of the nuclei.

The separation of all of the generalized coordinates in the system at hand into fast and slow components gives rise naturally to the concepts of channels (adiabatic states), adiabatic potentials (potential energy surfaces), and skew-Hermitian operators of nonadiabatic coupling. The adiabatic potentials and nonadiabatic coupling operators are functions of the slow variables. There are two basic classes of representations of the multichannel stationary Schrödinger equation (i.e., description schemes for the corresponding quantum mechanical system). These classes are (1) *diabatic representations* referring to the values of the slow coordinates at a fixed instant of the evolution of the system and (2) the unique *adiabatic representation* that relies upon the current values of the slow variables.[2−7]

Treating the nonadiabatic coupling operators as perturbations may lead in some cases to new representations of the multichannel stationary Schrödinger equation. Klar and Fano[8,9] noticed that in the case where the system is characterized by a *single* slow coordinate and the Hamilton operator is *real* the following can be done. For each value of the slow coordinate R, it is possible to include (using only algebraic operations) the nonadiabatic coupling matrix $P(R)$ in the adiabatic potential energy curves $u_1(R), \ldots, u_n(R)$ and obtain new post-adiabatic potentials $u_1^{(1)}(R), \ldots, u_n^{(1)}(R)$ and a new post-adiabatic coupling $\Pi_1(R)$, which may be, in a certain sense, smaller than the initial coupling $P(R)$. Henceforth, n denotes the number of channels to be taken into account. In turn, the residual coupling $\Pi_1(R)$ can be included for each value of R, again using algebraic operations only, in post-adiabatic potentials $u_k^{(1)}$, $1 \leq k \leq n$, yielding the post-adiabatic potentials $u_1^{(2)}(R), \ldots, u_n^{(2)}(R)$ of the second order and the post-adiabatic coupling $\Pi_2(R)$ of the second order, and so on. This iterative procedure of successively constructing the post-adiabatic potentials $u_1^{(s)}(R), \ldots, u_n^{(s)}(R)$ and couplings $\Pi_s(R)$ of orders $s = 1, 2, \ldots$ is formally infinite, although it is generically divergent (see section II below). The post-adiabatic potentials and post-adiabatic coupling of order $s \geq 1$ enter the *post-adiabatic representation* of the multichannel stationary Schrödinger equation of order s. As in the case of the conventional adiabatic representation, the post-adiabatic representations of all of the orders are connected with the current value of the slow coordinate R.

In the pioneering papers of the mid-1970s,[8−10] only the first step of the iterative procedure mentioned above, namely, obtaining the post-adiabatic potentials and couplings of the first

---

[†] Part of the "Gert D. Billing Memorial Issue".

* To whom correspondence should be sent. E-mail: rusin@chph.ras.ru, sevryuk@mccme.ru.

10.1021/jp040099m CCC: $27.50

order, was considered through the example of the scattering of an electron on a hydrogen atom. As the slow variable, the so-called Fock mean-square radius of the two electrons was used. In our previous publications on the subject,[4,5] all of the steps of this procedure were treated from a unified viewpoint, the algebraic structures underlying the post-adiabatic representations were clarified, and various special properties of these representations were discussed in detail. We also performed a post-adiabatic analysis of the van der Waals interactions of the fluorine, chlorine, and oxygen atoms with some closed-shell particles Z, namely, the rare-gas atoms and molecules of deuterium, methane, and hydrogen halides HCl, HBr, and HI. The theory founded by Klar et al.[8−10] and developed further in our work[4] was used in recent papers[11,12] to study the interaction between a Rydberg electron and an ionic core, the slow coordinate being the distance between the electron and the nucleus of the ion.

The aim of constructing post-adiabatic representations of multichannel Schrödinger equations is threefold.[13] First, in many cases, post-adiabatic couplings of low orders do turn out to be smaller than the initial nonadiabatic coupling P, which promises more accurate and faster integration of the Schrödinger equation. Second, comparing post-adiabatic couplings of different orders may help one to estimate the strength of the nonadiabatic effects in the system. For instance, one may conclude from the smallness of the first-order post-adiabatic coupling Π_1 that the nonadiabatic effects in the system in question (i.e., the probabilities of nonadiabatic transitions) are weak, even if the original nonadiabatic coupling P is not very small. Third, using the post-adiabatic potentials in simulations of the process (with the coupling neglected) in place of the adiabatic ones sometimes leads to better agreement with the experimental data. This is the case for the situations considered by Klar et al.[8−10] and Clark et al.[11,12]

The main goal of the present paper is to extend the post-adiabatic analysis of the interactions of the F, Cl, and O atoms with closed-shell particles presented in our previous articles[4,5] to the van der Waals interaction of the *sulfur* atom with rare-gas atoms. Such an analysis is of interest both from a practical viewpoint, taking into account the great importance of sulfur-containing compounds for combustion and atmospheric chemistry and their potential to damage the ecology of the earth's atmosphere,[14] and from the point of view of exploring the trends in the behavior of the post-adiabatic couplings, depending on the properties of the adiabatic potentials and the nonadiabatic couplings and the masses of the partners. Some preliminary results of the post-adiabatic approach to the S−Ne, −Ar, −Kr, and −Xe interactions have been reported.[15] We also address some more special questions such as the optimal way of comparing post-adiabatic couplings of different orders and a rigorous proof of the nonexistence of post-adiabatic representations for systems with several slow degrees of freedom.

The paper is organized as follows. In section II, we give a sketch of the Klar−Fano iterative procedure for deriving post-adiabatic representations of multichannel Schrödinger equations and recall some properties of these representations discussed in more detail previously.[5] The theoretical background for investigating the interactions of the F(^{2}P), Cl(^{2}P), O(^{3}P), and S(^{3}P) atoms with closed-shell particles Z and the results of our post-adiabatic analysis of the S−He, −Ne, −Ar, −Kr, and −Xe systems are presented in section III. The features of the first-order post-adiabatic coupling in all four series F−Z, Cl−Z, O−Z, and S−Z are surveyed in section IV. Conclusions follow in section V. Appendix A contains a proof of the impossibility of post-adiabatic representations for systems with more than one slow coordinate.

II. Post-Adiabatic Iterative Procedure

As was observed a decade ago,[4] the mathematical background for post-adiabatic representations of multichannel Schrödinger equations is the theory of Hamiltonian and symplectic matrices over real or complex numbers. Recall that a $2n \times 2n$ matrix K with complex entries is said to be *Hamiltonian* if

$$K^{\mathrm{t}}J + JK = 0$$

where

$$J = \begin{pmatrix} 0 & -I \\ I & 0 \end{pmatrix}$$

I denotes the $n \times n$ identity matrix, and the superscript t designates the matrix transposition. The Hamiltonian matrices determine Hamiltonian linear differential equations. A $2n \times 2n$ matrix K is Hamiltonian if and only if it has the form

$$K = \begin{pmatrix} A & B \\ C & -A^{\mathrm{t}} \end{pmatrix} \qquad (1)$$

with symmetric $n \times n$ blocks B and C ($B^{\mathrm{t}} = B$, $C^{\mathrm{t}} = C$) and an arbitrary $n \times n$ block A. A $2n \times 2n$ matrix S with complex entries is said to be *symplectic* if

$$S^{\mathrm{t}}JS = J$$

The symplectic matrices determine canonical linear transformations.

In the rich literature on the theory of Hamiltonian and symplectic matrices, we confine ourselves here to references to the landmark paper by Williamson,[16] where the so-called normal forms of the Hamiltonian matrices were derived for the first time, and to books by Arnold[17] and Bruno.[18] (The latter book contains an extensive bibliography.)

The adiabatic n-channel stationary Schrödinger equation in the case of a *single* slow variable R has the form[2−7]

$$-\frac{\hbar^2}{2\mu}\left(I\frac{\mathrm{d}}{\mathrm{d}R} + P\right)^2\Phi + U\Phi = E\Phi \qquad (2)$$

where $U(R)$ is the diagonal real $n \times n$ matrix whose diagonal entries $u_1(R), \ldots, u_n(R)$ are the adiabatic potentials, $P(R)$ is the skew-Hermitian $n \times n$ matrix of the nonadiabatic coupling, μ is the reduced mass (corresponding to the coordinate R), E denotes the total energy of the system, and $\Phi(R)$ is an n-dimensional vector of the coefficients at the adiabatic states. Recall that I is the $n \times n$ identity matrix. Equation 2 can be rewritten as

$$m\frac{\mathrm{d}}{\mathrm{d}R}\begin{pmatrix} \Phi \\ \Xi \end{pmatrix} + \left[\begin{pmatrix} 0 & I \\ U - EI & 0 \end{pmatrix} + m\begin{pmatrix} P & 0 \\ 0 & P \end{pmatrix}\right]\begin{pmatrix} \Phi \\ \Xi \end{pmatrix} = 0 \qquad (3)$$

where the coefficient m is

$$m = \frac{\hbar}{(2\mu)^{1/2}} \qquad (4)$$

and

$$\Xi = -m\left(\frac{\mathrm{d}\Phi}{\mathrm{d}R} + P\Phi\right) \qquad (5)$$

Suppose that the Hamilton operator of the system in question is real. (In the theory of atomic and molecular processes, this is almost always the case if the spin–orbit interaction is neglected, and often, although not always,[19,20] it holds in the presence of this interaction as well.) Then the $n \times n$ matrix P is real and skew-symmetric, the $2n \times 2n$ matrix

$$\Pi_0 = \begin{pmatrix} P & 0 \\ 0 & P \end{pmatrix} \tag{6}$$

is therefore Hamiltonian, and eq 3 can be used as the starting point for the hierarchy of the post-adiabatic representations of the stationary Schrödinger equation that we are studying. One may call eq 3 the zeroth-order post-adiabatic equation.

Now an iterative step of the procedure is performed as follows. The post-adiabatic n-channel stationary Schrödinger equation of any order $s \geq 0$ has the form[4,5]

$$m\frac{\mathrm{d}X}{\mathrm{d}R} + K_sX = 0 \qquad K_s = \begin{pmatrix} 0 & I \\ U_s - EI & 0 \end{pmatrix} + m\Pi_s \tag{7}$$

where $U_s(R)$ is a diagonal $n \times n$ matrix whose (generally speaking, complex) diagonal entries $u_1^{(s)}(R), \ldots, u_n^{(s)}(R)$ are the post-adiabatic potentials of order s (corresponding to the total energy E), $\Pi_s(R)$ is a (generally speaking, complex) Hamiltonian $2n \times 2n$ matrix of the post-adiabatic coupling of order s (corresponding to the total energy E), and $X(R)$ is a $2n$-dimensional vector. For $s = 0$, one sets

$$U_0 = U \qquad u_k^{(0)} = u_k \ (1 \leq k \leq n)$$

and the matrix Π_0 is defined by eq 6. It is obvious that the eigenvalues of the Hamiltonian $2n \times 2n$ matrix

$$Q_s = \begin{pmatrix} 0 & I \\ U_s - EI & 0 \end{pmatrix}$$

are

$$\pm[u_k^{(s)} - E]^{1/2} \qquad 1 \leq k \leq n$$

Taking into account that the eigenvalues of any Hamiltonian matrix come in pairs $\pm\lambda$,[16−18] let us denote the eigenvalues of the Hamiltonian $2n \times 2n$ matrix $K_s = Q_s + m\Pi_s$ by $\pm\lambda_1^{(s)}, \ldots, \pm\lambda_n^{(s)}$. The functions

$$u_1^{(s+1)}(R) = [\lambda_1^{(s)}(R)]^2 + E, \ldots, u_n^{(s+1)}(R) = [\lambda_n^{(s)}(R)]^2 + E$$

are called[4,5] the post-adiabatic potentials of order $s + 1$ (corresponding to the total energy E).

Denote by U_{s+1} the diagonal $n \times n$ matrix with diagonal entries $u_1^{(s+1)}, \ldots, u_n^{(s+1)}$. The Hamiltonian $2n \times 2n$ matrices K_s and

$$Q_{s+1} = \begin{pmatrix} 0 & I \\ U_{s+1} - EI & 0 \end{pmatrix} \tag{8}$$

have the same spectrum

$$\pm[u_k^{(s+1)} - E]^{1/2} \qquad 1 \leq k \leq n$$

If this spectrum for any value of R in a certain range is simple; in other words, if all of the n numbers $u_1^{(s+1)}(R), \ldots, u_n^{(s+1)}(R)$ are pairwise distinct and other than E, then the matrices $K_s(R)$ and $Q_{s+1}(R)$ are conjugated for each R in this range, at least over complex numbers, by a symplectic $2n \times 2n$ matrix $S_s(R)$:[16−18]

$$S_s^{-1}K_sS_s = Q_{s+1}$$

The $2n \times 2n$ matrix

$$\Pi_{s+1}(R) = S_s^{-1}\frac{\mathrm{d}S_s}{\mathrm{d}R} \tag{9}$$

is Hamiltonian[4,5] for each R and is called[4,5] the matrix of the post-adiabatic coupling of order $s + 1$ (corresponding to the total energy E). In many cases, the calculation of this matrix is facilitated greatly by the so-called symplectic Hellmann–Feynman theorem.[4] The coordinate transformation $X = S_sY$ with a $2n$-dimensional vector $Y(R)$ casts eq 7 as the equation

$$m\frac{\mathrm{d}Y}{\mathrm{d}R} + K_{s+1}Y = 0 \qquad K_{s+1} = \begin{pmatrix} 0 & I \\ U_{s+1} - EI & 0 \end{pmatrix} + m\Pi_{s+1} \tag{10}$$

which is called[4,5] the post-adiabatic n-channel stationary Schrödinger equation of order $s + 1$. Equation 10 has the same form as eq 7, but with U_{s+1} in place of U_s and Π_{s+1} in place of Π_s.

Simpler analogues of this construction were proposed (in different setups) by A. I. Neishtadt (published by Arnold[21]) and A. G. Chirkov[22] for quantum systems with slowly varying (i.e., depending on slow time $\tau = \epsilon t$, $0 < \epsilon \ll 1$) Hamilton operators. Instead of transforming the Schrödinger equation, Chirkov[22] considers successive approximations to its solutions. Interestingly, one of the approximations in Chirkov's theory is referred to in his paper[22] as the "postadiabatic approximation". Quantum[23,24] and classical[17,24,25] systems with slowly varying Hamilton operators or functions constitute the Ehrenfest framework for the adiabaticity theories, which is probably more familiar.[17,23−25]

In contrast to the conventional adiabatic representation (eq 2) of a multichannel stationary Schrödinger equation, the post-adiabatic representation of any order $s \geq 1$ obtained as explained above is not unique because the symplectic $2n \times 2n$ matrix S_s conjugating the Hamiltonian $2n \times 2n$ matrices K_s (eq 7) and Q_{s+1} (eq 8) is not determined uniquely. (In fact, for any fixed value of the slow variable R, the matrices S_s constitute a manifold of complex dimension n.) An unsuitable choice of S_s could lead to very large post-adiabatic coupling Π_{s+1} (eq 9) of order $s + 1$. We proposed[4] a simple algorithm for choosing S_s, which ensures a small coupling Π_{s+1} provided that the coupling Π_s of the previous order s was already sufficiently small. Moreover, as was proven in our subsequent paper,[5] the matrix $S_s(R)$ yielded by this algorithm keeps smoothness (as a function of R) at the so-called turning points R^*,[26] where $u_k^{(s+1)}(R^*) = E$ for some k, $1 \leq k \leq n$. In the sequel, the conjugating matrices S_s at each step of the post-adiabatic iteration procedure and at each value of the slow coordinate will always be assumed to be chosen according to our algorithm.[4] It is also important to emphasize that the post-adiabatic potentials and couplings depend on the reduced mass μ and on the total energy E.

The sequence of the post-adiabatic representations of a generic multichannel stationary Schrödinger equation of orders $s = 1, 2, \ldots$ diverges as $s \to \infty$.[27] The reason is the operation of differentiating the conjugating matrix with respect to R, which enters eq 9: the sth derivative of a typical holomorphic function grows like $s!$ as s increases[28] (the derivatives of nonholomorphic, infinitely differentiable functions grow, as a rule, much faster[29]), and this rapid growth becomes dominant for large s. In section

V below, we present this argument in more detail. Moreover, according to a recent paper by Kendrick et al.,[30] multichannel Schrödinger equations admit no representation for which the nonadiabatic terms are systematically (i.e., for most of the equations) smaller than the conventional nonadiabatic coupling. However, as we will see in section IV below, the first-order post-adiabatic coupling Π_1 is smaller than the usual nonadiabatic coupling P for a number of systems.

Nevertheless, a comparison of the post-adiabatic couplings of different orders is complicated greatly by the fact that the $n \times n$ blocks A_s, B_s, C_s of the $2n \times 2n$ matrix

$$\Pi_s = \begin{pmatrix} A_s & B_s \\ C_s & -A_s^{\mathrm{t}} \end{pmatrix} \qquad s \geq 1 \tag{11}$$

(cf. eq 1) are of *different physical dimensions*:[4,5]

$$\Pi_s \approx \begin{pmatrix} \text{length}^{-1} & \text{length}^{-1}\ \text{energy}^{-1/2} \\ \text{length}^{-1}\ \text{energy}^{1/2} & \text{length}^{-1} \end{pmatrix} \tag{12}$$

This circumstance makes it impossible to compare P (which is of dimension length^{-1}) and Π_s, $s = 1, 2, \ldots$, in a straightforward manner. In our previous papers,[4,5] we suggested multiplying the entries of the symmetric blocks B_s and C_s of the matrices Π_s by functions of the adiabatic potentials $u_1, \ldots, u_n$ to achieve a dimension of length^{-1}. This "palliative", despite its arbitrariness, is utilized in the present work as well (cf. eq 14 below). As an alternative remedy, one could deal with the dimensionless Schrödinger equation, which is of course equivalent to multiplying the block B_s in eq 11 by hartree$^{1/2}$ and block C_s by hartree$^{-1/2}$ (cf. eq 23 below). For the van der Waals interactions considered in the present paper, this second method of "dimension correction" always results in larger first-order post-adiabatic couplings as compared with the first method. (See section IV below.)

However, the most natural way to overcome the dimension problem just indicated is perhaps to measure the smallness of Π_s by the differences between the post-adiabatic potentials $u_1^{(s+1)}, \ldots, u_n^{(s+1)}$ of order $s + 1$ and the respective post-adiabatic potentials $u_1^{(s)}, \ldots, u_n^{(s)}$ of the previous order s. Indeed, if $\Pi_s = 0$ then $K_s = Q_s$ and $u_k^{(s+1)} = u_k^{(s)}$ for each $1 \leq k \leq n$, and the stronger the coupling Π_s, the larger the differences $|u_k^{(s+1)} - u_k^{(s)}|$. This approach to estimating the coupling strength can be equally applied to the conventional nonadiabatic coupling P (which corresponds to the differences $|u_k^{(1)} - u_k|$) and the post-adiabatic couplings Π_s of orders $s \geq 1$. Its usefulness will be justified further in section IV below.

Another complication of the post-adiabatic analysis is that the post-adiabatic potentials and coupling matrices can be complex in certain ranges of the slow variable R.[4,5] Nonetheless, nonreal potentials are widely used in the modern theory of elementary processes in, for example, the wave packet propagation techniques.[31]

We performed a detailed post-adiabatic analysis of the two-state problem ($n = 2$).[4,5] For $n = 2$, the matrix of the first-order post-adiabatic coupling has the form

$$\Pi_1 = S_0^{-1} \frac{\mathrm{d}S_0}{\mathrm{d}R} = \begin{pmatrix} x & 0 & 0 & z \\ 0 & y & z & 0 \\ 0 & t & -x & 0 \\ t & 0 & 0 & -y \end{pmatrix} \tag{13}$$

(cf. eqs 9 and 11). In particular, explicit expressions were derived for the first-order post-adiabatic potentials $u_1^{(1)}$ and $u_2^{(1)}$ and for the elements x, y, z, t of the first-order post-adiabatic coupling matrix Π_1 (eq 13) in terms of the adiabatic potentials u_1 and u_2, of the element p of the nonadiabatic coupling matrix

$$P = \begin{pmatrix} 0 & p \\ -p & 0 \end{pmatrix}$$

of the reduced mass μ of the system, and of the total energy E. We also determined under which conditions the first-order "post-adiabatic" potentials $u_1^{(1)}$ and $u_2^{(1)}$ and the transformation matrix S_0 are real.

It is worthwhile to note that the meaning of the term "post-adiabatic" used in some articles is quite different from the post-adiabaticity discussed in Klar et al.,[8−10] Aquilanti et al.,[4,5] Clark et al.,[11,12] and the present article. For instance, the post-adiabatic potentials of Nikitin et al.[32] are the eigenvalues of the matrix $U + \mathrm{i}cP$ (in our notation), where c is a certain real parameter. Such potentials are always real (provided that the coupling P is real) because the matrix $U + \mathrm{i}cP$ is Hermitian. The post-adiabatic potentials in the sense of Zhu et al.[33] are just the usual adiabatic potentials. In a number of papers by Berry et al.,[34−36] a hierarchy of corrections to the adiabatic approximation is studied in certain systems with classical slow variables and classical or quantum fast variables, and some of those corrections (e.g., the so-called geometric magnetism and deterministic friction) are sometimes referred to as post-adiabatic corrections.[35,36] However, such corrections have nothing in common with the post-adiabatic representations and potentials as introduced by Klar and Fano.[8]

For two-state systems with any number of slow degrees of freedom and real nonadiabatic coupling operators, Baer and Englman[37] proposed another construction of "including" nonadiabatic couplings in the adiabatic potentials, which was subsequently extended to a certain class of systems with an arbitrary number of states.[7,38] This construction is entirely different from the Klar−Fano approach and admits no iterations.

Finally, one should distinguish between the hierarchy of post-adiabatic representations of multichannel Schrödinger equations outlined above and the hierarchy of adiabatic separations of the variables.[39] The latter hierarchy appears in the case where all of the slow variables can be divided into moderately slow variables and very slow ones; then a similar procedure is carried out with respect to the very slow degrees of freedom and so on. A typical example (one of the three examples pointed out by Tolstikhin et al.[39]) is the Born−Oppenheimer[1] separation of fast electronic evolution from slow nuclear coordinates accompanied by a subsequent analysis of the nuclear motions by the hyperspherical coordinate method[3,39,40] and the separation of, for example, the very slow hyperradius from the moderately slow angular variables.

III. Post-Adiabatic Analysis of Rare-Gas Sulfides and Some Other Open-Shell Systems

The long-range van der Waals interaction of the F(^{2}P), Cl(^{2}P), O(^{3}P), and S(^{3}P) atoms with closed-shell (i.e., ^{1}S) particles Z has been extensively studied over the last 15 years from both theoretical and experimental viewpoints;[5,41−57] the appropriate angular momentum coupling schemes and decoupling approximations were developed earlier.[58−60] The nonadiabatic transitions in these systems are induced mainly by the radial relative motion of the partners; therefore, it makes sense to examine the interactions F−, Cl−, O−, and S−Z neglecting the rotations of the interparticle axis and treating the interparticle distance R as the only slow variable. In turn, this circumstance makes it possible to apply the post-adiabatic analysis to these systems.

The interaction between ^{1}S and ^{2}P particles gives rise to three adiabatic states $|j\Omega\rangle = |3/21/2\rangle$, $|3/23/2\rangle$, $|1/21/2\rangle$. (The state $|j\Omega\rangle$ correlates with the total angular momentum j of the species ^{2}P as $R \rightarrow \infty$ and is characterized by the projection Ω of the total angular momentum along the interparticle axis).[42,44−49,51,53,54,58,59,61] For the case of a $(p^5)(^2\text{P})$ atom (e.g., a halogen atom), the ground state is $|3/21/2\rangle$. States $|3/21/2\rangle$ and $|1/21/2\rangle$ with the same value of $\Omega = {}^1/_2$ are coupled and therefore constitute a two-state problem.

Similarly, the interaction between ^{1}S and ^{3}P particles gives rise to six adiabatic states $|j\Omega\rangle = |22\rangle$, $|21\rangle$, $|20\rangle$, $|11\rangle$, $|10\rangle$, $|00\rangle$.[41,43,44,50,52,56−58,60] This collection of states turns out to constitute two mutually uncoupled two-state problems $|20\rangle$, $|00\rangle$ (the problem with $\Omega = 0$) and $|21\rangle$, $|11\rangle$ (the problem with $\Omega = 1$), but the coupling between each of the states $|22\rangle$, $|10\rangle$ and any of the remaining five states vanishes. For the case of a $(p^4)(^3\text{P})$ atom (e.g., the oxygen, sulfur, selenium, or tellurium atom), the ground state is $|22\rangle$.

The adiabatic potentials $V_{|j\Omega\rangle}(R)$ for all the three states $|j\Omega\rangle$ and the matrix element $p_{1/2}(R)$ of the nonadiabatic coupling between the $|3/21/2\rangle$ and $|1/21/2\rangle$ states have been experimentally determined for 10 systems F(^{2}P)−Z, namely, F−He, −Ne, $-D_2$, $-CH_4$,[45] F−Ar, −Kr, −Xe,[42] F−HCl, −HBr, and −HI,[46] and 7 systems Cl(^{2}P)−Z, namely, Cl−He, −Ne, −Ar, −Kr,[48] −Xe,[47] $-D_2$, and $-CH_4$.[49] The adiabatic potentials $V_{|j\Omega\rangle}(R)$ for all six states $|j\Omega\rangle$, the matrix element $p_0(R)$ of the nonadiabatic coupling between the $|20\rangle$ and $|00\rangle$ states, and the matrix element $p_1(R)$ of the nonadiabatic coupling between the $|21\rangle$ and $|11\rangle$ states have been experimentally determined for seven systems O(^{3}P)−Z, namely, O−He, −Ne, −Ar, −Kr, −Xe,[41] $-D_2$, and $-CH_4$,[43] and four systems S(^{3}P)−Z, namely, S−Ne, −Ar, −Kr, and −Xe.[52] In all of the cases, the indicated features of the long-range intermolecular interaction were found by analyzing the elastic differential and integral cross sections (first, the glory structure in the integral cross sections) measured by molecular beam techniques. The experiments were performed in the Göttingen group for systems F−HCl, −HBr, and −HI[46] and in the Perugia group for all of the other systems. Molecules D_2, CH_4, HCl, HBr, and HI were treated as spherically symmetric ^{1}S particles, although this approximation is probably not very good for such strongly anisotropic molecules as HCl and HBr. Experimental data for the S−He system are absent. However, accurate ab initio adiabatic potentials $V_{|j\Omega\rangle}(R)$ and the corresponding nonadiabatic coupling matrix elements $p_{1/2}(R)$, $p_0(R)$, and $p_1(R)$ have recently become available for rare-gas fluorides,[53,55,62] chlorides,[51,53,54,62] oxides,[50,56,62] and sulfides.[50,57,62] In fact, for both types of systems (^{2}P−Z and ^{3}P−Z), all of the adiabatic potentials and nonadiabatic coupling matrix elements mentioned above can be expressed in terms of the eigenvalues $V_\Sigma(R)$ and $V_\Pi(R)$ of the electrostatic Hamilton operator (diabatic potentials) and the fine-splitting constant(s) of the open-shell atom.

Around the ground-state potential minimum, the interaction in the systems studied can be described by an atomic coupling scheme (Hund's case (*c*)) for light closed-shell species (weaker interactions) and by a molecular coupling scheme [Hund's case (*a*)] for heavy closed-shell species (stronger interactions).[44,58,63]

We have performed a post-adiabatic analysis of 45 two-state problems arising from interactions F(^{2}P)−Z, with Z = He, Ne, Ar, Kr, Xe, H_2, D_2, CH_4, HCl, HBr, HI; Cl(^{2}P)−Z, with Z = He, Ne, Ar, Kr, Xe, H_2, D_2, CH_4; O(^{3}P)−Z, Z = He, Ne, Ar, Kr, Xe, H_2, D_2, CH_4; and S(^{3}P)−Z, Z = He, Ne, Ar, Kr, Xe. To each of the 19 systems F−Z and Cl−Z, there corresponds a single two-state problem with adiabatic potentials

$$u_1 = V_{|1/21/2\rangle} \qquad u_2 = V_{|3/21/2\rangle}$$

and nonadiabatic coupling matrix element $p_{1/2}$. To each of the 13 systems O−Z and S−Z, there corresponds a pair of two-state problems: the problem for $\Omega = 0$ and that for $\Omega = 1$. The $\Omega = 0$ problem is characterized by adiabatic potentials

$$u_1 = V_{|00\rangle} \qquad u_2 = V_{|20\rangle}$$

and nonadiabatic coupling matrix element p_0. The $\Omega = 1$ problem is characterized by adiabatic potentials

$$u_1 = V_{|11\rangle} \qquad u_2 = V_{|21\rangle}$$

and nonadiabatic coupling matrix element p_1. In all cases, $u_1(R) > u_2(R)$ for all values of R.

For each of these 45 two-state problems for $1.25 \leq R \leq 7$ Å with a step of 0.001 Å, we have calculated first-order post-adiabatic potentials $u_1^{(1)}(R)$ and $u_2^{(1)}(R)$, elements $x(R)$, $y(R)$, $z(R)$, and $t(R)$ of the first-order post-adiabatic coupling matrix Π_1 (eq 13), and second-order post-adiabatic potentials $u_1^{(2)}(R)$ and $u_2^{(2)}(R)$ for four values of the total energy $E = -50$, 25, 100, and 200 meV. For each problem, the zero value of the total energy was fixed by the condition that $u_2(R) \rightarrow 0$ as $R \rightarrow \infty$, this condition being equivalent to requiring that the ground-state potential of the system under consideration vanish at $R = \infty$. The values $E = 25$, 100, and 200 meV lie in the experimentally observable range of collision energies. The value $E = -50$ meV corresponds to a bound motion in the potential well (if its depth exceeds 50 meV). For the adiabatic potentials and nonadiabatic coupling matrix elements, we used ab initio curves in the case of the S−He interaction[57] and experimentally derived functions for all of the other systems.[41−43,45−49,52] For the interactions of the F, Cl, and O atoms with the hydrogen molecule H_2, the same adiabatic potentials and nonadiabatic coupling matrix elements were exploited as for the respective interactions of these atoms with the deuterium molecule D_2. The post-adiabatic potentials and coupling matrices are nonetheless dependent on the reduced mass μ of the two partners, and these potentials and matrices were therefore different for the H_2 and D_2 species.

The minimal value (1.25 Å) of the interparticle distance R that we probed was chosen by taking into account the observation that at smaller distances R the potential models we used for Cl−He[48] and S−He[57] become inadequate (concerning the Cl−He case, cf. Table 3, the $R_{\tilde{z},\tilde{t}}$ column, and Figure 5 of our previous publication[5]).

In all cases, we considered the "dimension-corrected" elements

$$x, \quad y, \quad \tilde{z} = \left[\frac{1}{2}(u_1 - u_2)\right]^{1/2} z, \quad \tilde{t} = \left[\frac{1}{2}(u_1 - u_2)\right]^{-1/2} t \tag{14}$$

of the first-order post-adiabatic coupling matrix Π_1 (eq 13). The dimension of all four quantities $x, y, \tilde{z}, \tilde{t}$ and of the nonadiabatic coupling matrix element p is length^{-1} (eq 12).

The experimental data on the scattering of S on D_2 obtained recently in the Perugia group[64] are rather preliminary and have therefore not been used in the present post-adiabatic analysis. We do not discuss various 2D and 3D potential energy surfaces (PESs) that are available for the interactions between the F, Cl, O, and S atoms and the H_2, HCl, HBr, and HI molecules and multidimensional (at most 12-dimensional) PESs for the interac-

TABLE 1: Results of the Post-Adiabatic Analysis of the Two-State Problems Constituted by States $|00\rangle$ and $|20\rangle$ of Rare-Gas Sulfides[a]

p^*, Å^{-1}	E, meV	$\max\{\delta^*_1, \delta^*_2\}$, meV	$\tilde{t}^*$, Å^{-1}	$\max\{\Delta^*_1, \Delta^*_2\}$, meV
He	−50	$\delta^*_1 = 6.37$	1.39	$\Delta^*_1 = 2.54$
	25	$\delta^*_1 = 3.61$	0.839	$\Delta^*_1 = 0.651$
1.09	100	$\delta^*_1 = 1.58$	0.832	$\Delta^*_2 = 0.274$
	200	$\delta^*_2 = 4.40$	1.34	$\Delta^*_2 = 1.16$
Ne	−50	$\delta^*_1 = 2.04$	0.832	$\Delta^*_1 = 0.235$
	25	$\delta^*_1 = 1.40$	0.679	$\Delta^*_1 = 0.109$
1.05	100	$\delta^*_1 = 0.878$	0.698	$\Delta^*_1 = 0.0462$
	200	$\delta^*_2 = 1.01$	0.927	$\Delta^*_2 = 0.110$
Ar	−50	$\delta^*_1 = 0.942$	0.392	$\Delta^*_1 = 0.0428$
	25	$\delta^*_1 = 0.481$	0.266	$\Delta^*_1 = 0.00925$
1.07	100	$\delta^*_2 = 0.428$	0.397	$\Delta^*_2 = 0.0168$
	200	$\delta^*_2 = 1.08$	0.693	$\Delta^*_2 = 0.0739$
Kr	−50	$\delta^*_1 = 0.695$	0.326	$\Delta^*_1 = 0.0228$
	25	$\delta^*_1 = 0.344$	0.233	$\Delta^*_1 = 0.00466$
1.08	100	$\delta^*_2 = 0.365$	0.366	$\Delta^*_2 = 0.0115$
	200	$\delta^*_2 = 0.874$	0.634	$\Delta^*_2 = 0.0484$
Xe	−50	$\delta^*_1 = 0.610$	0.297	$\Delta^*_1 = 0.0172$
	25	$\delta^*_1 = 0.285$	0.205	$\Delta^*_1 = 0.00294$
1.09	100	$\delta^*_2 = 0.357$	0.343	$\Delta^*_2 = 0.00985$
	200	$\delta^*_2 = 0.829$	0.608	$\Delta^*_2 = 0.0423$

[a] Functions $\delta_k(R)$, $\Delta_k(R)$, and $\tilde{t}(R)$ are defined by eqs 16, 17, and 14, respectively, and $p(R)$ is the non-adiabatic coupling matrix element. The asterisk means the maximum of the absolute value over the range $1.25 \le R \le 7$ Å.

TABLE 2: Results of the Post-Adiabatic Analysis of the Two-State Problems Constituted by States $|11\rangle$ and $|21\rangle$ of Rare-Gas Sulfides[a]

p^*, Å^{-1}	E, meV	$\max\{\delta^*_1, \delta^*_2\}$, meV	$\tilde{t}^*$, Å^{-1}	$\max\{\Delta^*_1, \Delta^*_2\}$, meV
He	−50	$\delta^*_1 = 2.89$	0.730	$\Delta^*_1 = 0.738$
	25	$\delta^*_1 = 1.33$	0.409	$\Delta^*_1 = 0.120$
0.779	100	$\delta^*_2 = 1.35$	0.660	$\Delta^*_2 = 0.249$
	200	$\delta^*_2 = 3.37$	1.16	$\Delta^*_2 = 1.06$
Ne	−50	$\delta^*_1 = 0.863$	0.401	$\Delta^*_1 = 0.0632$
	25	$\delta^*_1 = 0.505$	0.341	$\Delta^*_1 = 0.0225$
0.749	100	$\delta^*_2 = 0.328$	0.475	$\Delta^*_2 = 0.0269$
	200	$\delta^*_2 = 0.865$	0.737	$\Delta^*_2 = 0.0960$
Ar	−50	$\delta^*_1 = 0.420$	0.200	$\Delta^*_1 = 0.0125$
	25	$\delta^*_1 = 0.158$	0.154	$\Delta^*_1 = 0.00226$
0.764	100	$\delta^*_2 = 0.367$	0.329	$\Delta^*_2 = 0.0158$
	200	$\delta^*_2 = 0.778$	0.586	$\Delta^*_2 = 0.0618$
Kr	−50	$\delta^*_1 = 0.307$	0.161	$\Delta^*_1 = 0.00643$
	25	$\delta^*_1 = 0.110$	0.144	$\Delta^*_1 = 0.00144$
0.770	100	$\delta^*_2 = 0.306$	0.306	$\Delta^*_2 = 0.0108$
	200	$\delta^*_2 = 0.628$	0.536	$\Delta^*_2 = 0.0403$
Xe	−50	$\delta^*_1 = 0.273$	0.149	$\Delta^*_1 = 0.00499$
	25	$\delta^*_1 = 0.0898$	0.133	$\Delta^*_2 = 0.00118$
0.781	100	$\delta^*_2 = 0.294$	0.294	$\Delta^*_2 = 0.00946$
	200	$\delta^*_2 = 0.593$	0.520	$\Delta^*_2 = 0.0353$

[a] The notation is the same as in Table 1.

tions between these atoms and the methane molecule because such potentials cannot be used straightforwardly within the post-adiabatic iteration scheme. As an example, we mention the 3D ab initio Alexander−Stark−Werner PESs[20] for the F + H_2 system, the subsequent 2D[65] and 3D[66] PESs for this system with the improved long-range region, and very recent 3D ab initio diabatic PESs for the F + H_2 van der Waals complex.[67]

The results of the post-adiabatic analysis of the interactions of the fluorine, chlorine, and oxygen atoms with closed-shell particles (without the value $E = 200$ meV of the total energy and without computing the second-order post-adiabatic potentials) were reported in our previous article[5] for all of the closed-shell species except H_2. The most important results of the post-adiabatic analysis of the interactions of the *sulfur* atom with rare-gas atoms are presented in Table 1 (for the $\Omega = 0$ two-state problems) and Table 2 (for the $\Omega = 1$ two-state problems). For rare-gas sulfides, the maximal values

$$x^* = \max_R |x(R)| \qquad y^* = \max_R |y(R)|$$
$$\tilde{z}^* = \max_R |\tilde{z}(R)| \qquad \tilde{t}^* = \max_R |\tilde{t}(R)|$$

of the dimension-corrected elements of the first-order post-adiabatic coupling matrix Π_1 in all cases (i.e., for the five closed-shell atoms, each of the two values of Ω, and each of the four values of the total energy E sampled) satisfy the inequalities

$$x^* < y^* < \tilde{z}^* < \tilde{t}^* \tag{15}$$

In Tables 1 and 2, we list (i) the maximal value

$$p^* = \max_R |p(R)|$$

of the corresponding nonadiabatic coupling matrix element p, (ii) the maximal value

$$\max\{\delta^*_1, \delta^*_2\} \qquad \delta^*_k = \max_R |\delta_k(R)|$$

of the differences

$$\delta_k(R) = u_k^{(1)}(R) - u_k(R) \qquad k = 1, 2 \tag{16}$$

between the first-order post-adiabatic potentials and the adiabatic potentials, (iii) the maximal value $\tilde{t}^*$ of the dimension-corrected element $\tilde{t}$ of the first-order post-adiabatic coupling matrix Π_1 (according to eq 15, this is also the maximal value of *all* four dimension-corrected elements of Π_1), and (iv) the maximal value

$$\max\{\Delta^*_1, \Delta^*_2\} \qquad \Delta^*_k = \max_R |\Delta_k(R)|$$

of the differences

$$\Delta_k(R) = u_k^{(2)}(R) - u_k^{(1)}(R) \qquad k = 1, 2 \tag{17}$$

between the second-order post-adiabatic potentials and the first-order post-adiabatic potentials. The notation $\max_R$ here means the maximum over the range $1.25 \le R \le 7$ Å of the internuclear distance R.

The behavior of the nonadiabatic and first-order post-adiabatic coupling matrix elements and the differences given by eqs 16 and 17 as functions of R for rare-gas sulfides is shown in Figures 1−3. The nonadiabatic coupling matrix element $p(R)$ possesses a single maximum in all cases. However, there are three behavior patterns for the differences $\delta_k(R)$ between the first-order post-adiabatic potentials and the adiabatic potentials: each function δ_1 and δ_2 has a single extremum (Figure 1), each of these functions exhibits two extrema (Figure 2), one of these functions has a single extremum, and the other one has two extrema (Figure 3). Here we take into account well-pronounced extrema only. The first pattern is typical for $E = 200$ meV and especially for $E = -50$ meV; the second and third patterns, for $E = 25$ and 100 meV. The behavior of the first-order post-adiabatic coupling matrix elements x, y, $\tilde{z}$, $\tilde{t}$ is usually more complicated than that of p, and the behavior of the differences Δ_k is more complicated than that of δ_k. An interesting topic for further work would be to compare the vibrational levels corresponding to the adiabatic potentials and the first-order post-adiabatic potentials.

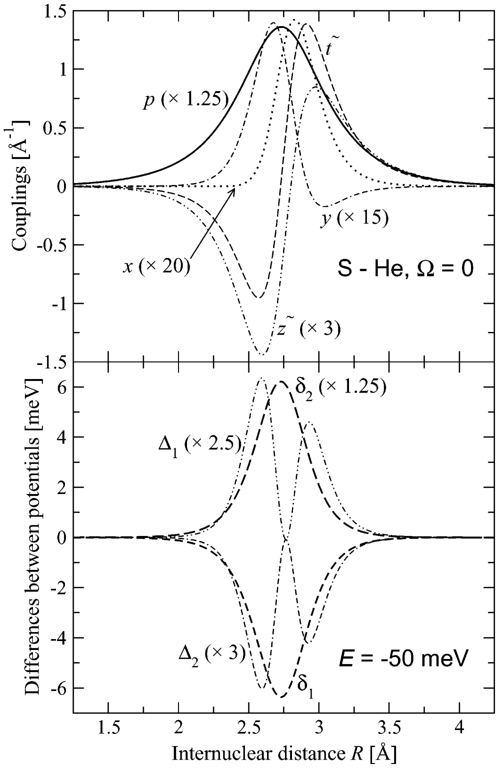

Figure 1. (Upper panel) nonadiabatic (p) and first-order post-adiabatic (x, y, $\tilde{z}$, $\tilde{t}$; eq 14) coupling matrix elements for the S−He interaction (the $\Omega = 0$ two-state problem) at a total energy E of −50 meV. (Lower panel) differences between the first-order post-adiabatic potentials and the adiabatic potentials ($\delta_{1,2}$; eq 16) and differences between the second-order and first-order post-adiabatic potentials ($\Delta_{1,2}$; eq 17) for the same two-state problem at the same value of E.

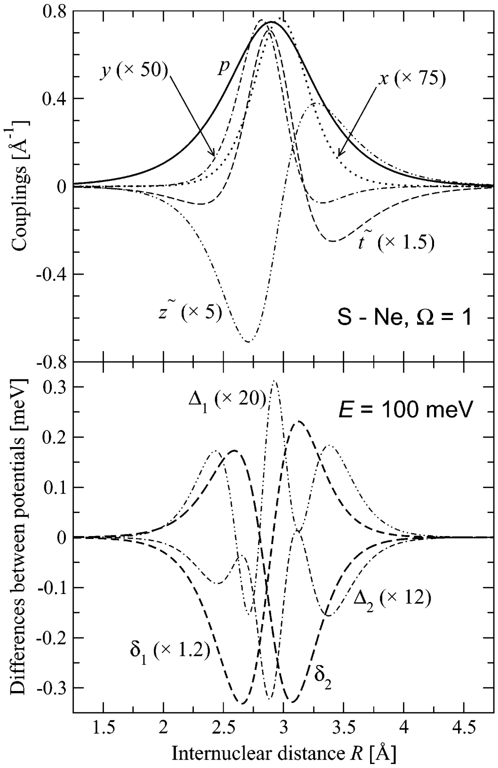

Figure 2. Nonadiabatic and first-order post-adiabatic coupling matrix elements (upper panel), the differences between the first-order post-adiabatic potentials and the adiabatic potentials, and the differences between the second-order and first-order post-adiabatic potentials (lower panel) for the S−Ne interaction (the $\Omega = 1$ two-state problem) at a total energy of 100 meV. The notation is the same as in Figure 1.

IV. Trends in the Post-Adiabatic Potentials and Couplings

In this section, we report general trends in the properties of the post-adiabatic potentials and couplings observed while examining all four series F−Z, Cl−Z, O−Z, and S−Z of open-shell systems that we have considered. Some of these trends were briefly discussed in our previous paper[5] for the first three series F−Z, Cl−Z, and O−Z.

In 42 two-state problems of the total number of 45 that we dealt with, the first-order post-adiabatic potentials $u_k^{(1)}$, the first-order post-adiabatic coupling matrix Π_1, and the second-order post-adiabatic potentials $u_k^{(2)}$ were real for all values of R in the range $1.25 \leq R \leq 7$ Å for all four values $E = -50$, 25, 100, and 200 meV of the total energy E. The only exceptions were the interactions O−He for $\Omega = 0$, O−H$_2$ for $\Omega = 0$, and O−H$_2$ for $\Omega = 1$ at $E = -50$ meV. For these three two-state problems at the lowest value, −50 meV, of the total energy, the potentials $u_k^{(1)}$ are complex for $2.451 \leq R \leq 2.704$ Å, $2.739 \leq R \leq 3.113$ Å, and $3.021 \leq R \leq 3.146$ Å, respectively.

For each of the six series of two-state problems that we have studied, F−Z, Cl−Z, O−Z ($\Omega = 0$), O−Z ($\Omega = 1$), S−Z ($\Omega = 0$), and S−Z ($\Omega = 1$), the first-order post-adiabatic coupling Π_1 (eq 13) and the differences δ_k (eq 16) and Δ_k (eq 17) decrease in general as the mass of the closed-shell species increases. This is caused by the growth of the reduced mass of the partners and partially by an increase in the potential well depth for the adiabatic potential u_2.[41−43,45,46,48,49,51−54,56,57,60]

In general, the first-order post-adiabatic coupling Π_1 and the differences δ_k and Δ_k for the O−Z systems are much larger than those for the S−Z systems (for both values of Ω), those for the S−Z systems are slightly larger than those for the F−Z systems, and those for the F−Z systems are larger than those for the Cl−Z systems. The main reason is that the first-order post-adiabatic coupling Π_1 for a two-state problem is very sensitive to the difference $u_1 - u_2$ between the adiabatic potentials, and the larger this difference, the weaker the coupling.[4,5] For the systems that we have explored, the difference $u_1 - u_2$ is determined primarily by the fine-splitting constants of the open-shell partner (and coincides with the corresponding constant at $R = \infty$). These constants are[68]

$$\begin{aligned}
&[\mathrm{F}(^2\mathrm{P}_{1/2})] - [\mathrm{F}(^2\mathrm{P}_{3/2})] = 50.1\ \mathrm{meV}\\
&[\mathrm{Cl}(^2\mathrm{P}_{1/2})] - [\mathrm{Cl}(^2\mathrm{P}_{3/2})] = 109.4\ \mathrm{meV}\\[6pt]
&[\mathrm{O}(^3\mathrm{P}_0)] - [\mathrm{O}(^3\mathrm{P}_2)] = 28.14\ \mathrm{meV}\\
&[\mathrm{O}(^3\mathrm{P}_1)] - [\mathrm{O}(^3\mathrm{P}_2)] = 19.62\ \mathrm{meV}\\[6pt]
&[\mathrm{S}(^3\mathrm{P}_0)] - [\mathrm{S}(^3\mathrm{P}_2)] = 71.12\ \mathrm{meV}\\
&[\mathrm{S}(^3\mathrm{P}_1)] - [\mathrm{S}(^3\mathrm{P}_2)] = 49.1\ \mathrm{meV}
\end{aligned} \tag{18}$$

where the brackets denote the energy of the corresponding atomic term. For the oxygen and sulfur atoms, the $^3\mathrm{P}_0 - {}^3\mathrm{P}_2$ and the $^3\mathrm{P}_1 - {}^3\mathrm{P}_2$ splittings are relevant for the two-state problems with $\Omega = 0$ and 1, respectively.

More precisely, consider the four closed-shell species Ne, Ar, Kr, and Xe for which the adiabatic potentials and the nonadiabatic coupling matrix elements have been determined experimentally for the four open-shell atoms F, Cl, O, and S.[41,42,45,47,48,52] Let f be any of the eight functions x, y, $\tilde{z}$, $\tilde{t}$ (eq 14), δ_1, δ_2 (eq 16), Δ_1, and Δ_2 (eq 17). For each of the 24 two-state problems F−Z, Cl−Z, O−Z ($\Omega = 0$), O−Z ($\Omega = 1$),

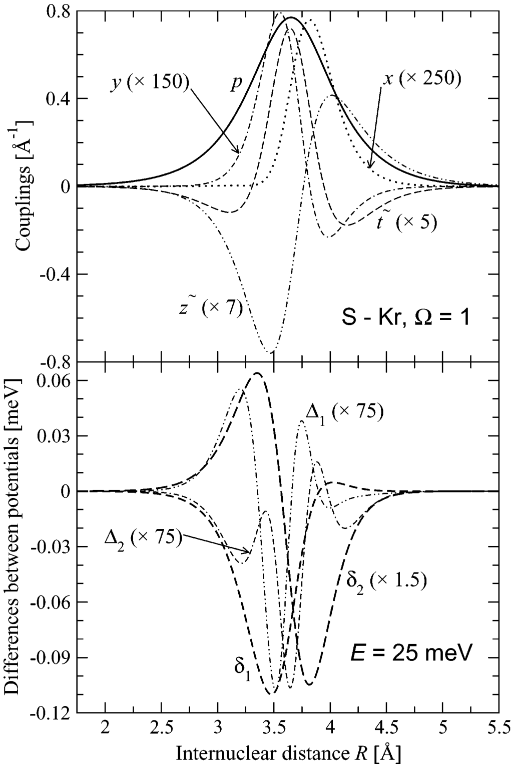

Figure 3. Nonadiabatic and first-order post-adiabatic coupling matrix elements (upper panel), the differences between the first-order post-adiabatic potentials and the adiabatic potentials, and the differences between the second-order and first-order post-adiabatic potentials (lower panel) for the S−Kr interaction (the Ω = 1 two-state problem) at a total energy of 25 meV. The notation is the same as in Figure 1.

S−Z (Ω = 0), S−Z (Ω = 1) with Z = Ne, Ar, Kr, or Xe, consider the quantity f_{mean} to be equal to the geometric mean of the maximal values $f^* = \max_R|f(R)|$ of $|f|$ over the four total energies E sampled:

$$f_{\text{mean}} = (f^*|_{E=-50\text{ meV}} \cdot f^*|_{E=25\text{ meV}} \cdot f^*|_{E=100\text{ meV}} \cdot f^*|_{E=200\text{ meV}})^{1/4}$$

It turns out that if for each of the 4 atoms Ne, Ar, Kr, and Xe and for each of the 8 functions f one arranges the corresponding 6 two-state problems in ascending order of f_{mean}, then as a rule (in 23 cases), one would obtain the sequence

$$\text{Cl} \to \text{F} \to \text{S}(\Omega = 1) \to \text{S}(\Omega = 0) \to \text{O}(\Omega = 1) \to \text{O}(\Omega = 0)$$

The exceptions are six functions $f \equiv x, y, \tilde{t}, \delta_1, \Delta_1, \Delta_2$ for Z = Ne and two functions $f \equiv \tilde{z}, \Delta_1$ for Z = Xe, where the corresponding sequence is

$$\text{Cl} \to \text{S}(\Omega = 1) \to \text{F} \to \text{S}(\Omega = 0) \to \text{O}(\Omega = 1) \to \text{O}(\Omega = 0)$$

as well as the function $f \equiv x$ for Z = Xe, where the sequence is

$$\text{Cl} \to \text{F} \to \text{S}(\Omega = 1) \to \text{O}(\Omega = 1) \to \text{S}(\Omega = 0) \to \text{O}(\Omega = 0) \tag{19}$$

Note that although the $^3P_0 - {}^3P_2$ fine-splitting constant for the oxygen and sulfur atoms is larger than the $^3P_1 - {}^3P_2$ fine-splitting constant (see eq 18), the Ω = 0 first-order post-adiabatic coupling for these open-shell species turns out to be larger than the Ω = 1 first-order post-adiabatic coupling for each closed-shell partner Z. The reason is that the Ω = 0 nonadiabatic coupling p_0 for these systems is larger than the Ω = 1 nonadiabatic coupling p_1;[41,52] cf. Tables 1 and 2 for the case of the S−Z interactions. If for a fixed rare-gas atom Ne, Ar, Kr, or Xe one arranges the corresponding six two-state problems in ascending order of $p^* = \max_R|p(R)|$, then one would obtain the sequence given by eq 19 for Ne and Ar and the sequence

$$\text{Cl} \to \text{F} \to \text{O}(\Omega = 1) \to \text{S}(\Omega = 1) \to \text{O}(\Omega = 0) \to \text{S}(\Omega = 0)$$

for Kr and Xe.

The dependence of the first-order post-adiabatic coupling Π_1 and the differences δ_k and Δ_k on the total energy E of the system (in the range $-50 \le E \le 200$ meV) is much stronger for the O−Z systems (for both values of Ω) than for the F−Z, Cl−Z, and S−Z systems.

Of the 45 two-state problems that we have studied, consider 42 problems for which the first-order post-adiabatic potentials are real for all R at each of the 4 values of E. (As was pointed out above, the three problems that do not satisfy this condition are O−He with Ω = 0, O−H$_2$ with Ω = 0, and O−H$_2$ with Ω = 1.) For each of the 8 functions $f \equiv x, y, \tilde{z}, \tilde{t}$ (eq 14), δ_1, δ_2 (eq 16), Δ_1, and Δ_2 (eq 17) and any of these 42 problems, arrange those 4 values of $E = -50, 25, 100, 200$ meV in ascending order of the maximum $f^* = \max_R|f(R)|$. It turns out that for the functions x, y, and $\tilde{z}$ one would obtain the sequence

$$200 \to 100 \to 25 \to -50 \text{ meV} \tag{20}$$

in all 42 problems (the lower E, the larger f^*). For each of the functions $\tilde{t}$, δ_2, and Δ_2, in most of the problems (to be more precise, in 31, 24, and 22 problems, respectively), one obtains the sequence

$$25 \to -50 \to 100 \to 200 \text{ meV}$$

Finally, for the functions δ_1 and Δ_1, the most frequent sequence of the values of E (obtained in 19 and 15 problems, respectively) is

$$25 \to 100 \to -50 \to 200 \text{ meV}$$

Return now to the question of comparing the nonadiabatic couplings and the first-order post-adiabatic couplings. Recall that we have examined 45 two-state problems for 4 values of the total energy E each (i.e., altogether 180 cases, of which in 3 cases the first-order post-adiabatic potentials are complex for some distances R). These three exceptional cases are O−He for Ω = 0, O−H$_2$ for Ω = 0, and O−H$_2$ for Ω = 1 at $E = -50$ meV. Of the remaining 177 cases, in 97 cases the inequalities

$$x^* < y^* < \tilde{z}^* < \tilde{t}^* < p^* \qquad \max\{\Delta^*_1, \Delta^*_2\} < \min\{\delta^*_1, \delta^*_2\}$$

hold (Figures 2 and 3), where, as before, the asterisk means the maximum of the absolute value over the interval $1.25 \le R \le 7$ Å. The minimal value of the ratio

$$G_1 = \frac{p^*}{\max\{x^*, y^*, \tilde{z}^*, \tilde{t}^*\}} \tag{21}$$

(equal in these cases to $p^*/\tilde{t}^*$) over the whole collection of 97 cases in question is 1.017, the maximal value is 12.577 (for Cl−Kr at $E = -50$ meV), and the mean value is 3.023. The minimal value of the ratio

$$G_2 = \frac{\min\{\delta^*_1, \delta^*_2\}}{\max\{\Delta^*_1, \Delta^*_2\}} \tag{22}$$

over this collection is 2.491, the maximal value is 180.439 (for

Cl−Kr at $E = 100$ meV), and the mean value is 23.472. There is a well-pronounced trend of an increase in the ratio G_2 as the ratio G_1 increases. The correlation coefficient[69] between these two ratios over all 97 cases in question is equal to 0.880.

In 16 cases (including only interactions F−Z and Cl−Z) of the 177 ones pointed out above, the inequalities

$$x^* < y^* < \tilde{t}^* < \tilde{z}^* < p^* \qquad \max\{\Delta^*_1, \Delta^*_2\} < \min\{\delta^*_1, \delta^*_2\}$$

hold. The minimal value of the ratio G_1 (eq 21) over these cases is 2.014 (note that this ratio is equal to $p^*/\tilde{z}^*$ in the cases in question), the maximal value is 12.913 (for Cl−Kr at $E = 25$ meV), and the mean value is 7.718. The minimal value of the ratio G_2 (eq 22) over these 16 cases is 3.611, the maximal value is 174.301 (again for Cl−Kr at $E = 25$ meV), and the mean value is 63.241. The trend of an increase in the ratio G_2 as the ratio G_1 increases is pronounced for these 16 cases, even better than for the 97 cases discussed before: the corresponding correlation coefficient[69] is equal to 0.916.

Thus, in 113 cases of the total number of 177 cases, ratios G_1 and G_2 both exceed 1. In these 113 cases, the first-order post-adiabatic coupling is indeed smaller (sometimes an order of magnitude smaller) than the conventional nonadiabatic coupling, within the framework of the dimension correction of eq 14. The differences between the post-adiabatic potentials of the second and first orders in these cases are also smaller than the differences between the first-order post-adiabatic potentials and the adiabatic potentials (sometimes more than 2 orders of magnitude smaller and more than an order of magnitude smaller on average).

In 47 cases of 177, the inequalities

$$x^* < y^* < \tilde{z}^* < p^* < \tilde{t}^* \qquad \max\{\Delta^*_1, \Delta^*_2\} < \min\{\delta^*_1, \delta^*_2\}$$

hold (Figure 1); consequently, the ratio G_1 (eq 21), equal to $p^*/\tilde{t}^*$ in these cases, is less than 1. This means that the first-order post-adiabatic coupling (dimension corrected according to eq 14) exceeds the nonadiabatic coupling. The minimal value of the ratio G_1 over the collection of the 47 cases in question is 0.275, the maximal value is 0.992, and the mean value is 0.576. However, the ratio G_2 (eq 22) for these cases is still greater than 1 (i.e., the differences between the post-adiabatic potentials of the second and first orders are still smaller than the differences between the first-order post-adiabatic potentials and the adiabatic potentials). This means that using the first-order post-adiabatic two-channel Schrödinger equation instead of the adiabatic Schrödinger equation still makes sense in the cases in question. The minimal value of the ratio G_2 over these 47 cases is 1.001, the maximal value is 4.796 (for F−Ne at $E = 200$ meV), and the mean value is 2.266. The correlation coefficient[69] between the ratios G_1 and G_2 for these cases is equal to 0.431.

Finally, in 17 cases (including only interactions of the F and O atoms with closed-shell species He, Ne, H_2, and D_2) of the total number of 177, the ratios G_1 (eq 21) and G_2 (eq 22) both turn out to be smaller than 1; in particular, the inequality $\min\{\delta_1^*, \delta_2^*\} < \max\{\Delta_1^*, \Delta_2^*\}$ holds. In these cases, using the first-order post-adiabatic representation of the corresponding two-channel Schrödinger equation makes no sense. However, the trend of an increase in the ratio G_2 as the ratio G_1 increases takes place in these cases as well: the corresponding correlation coefficient[69] is equal to 0.709. In 10 cases of these 17, the inequalities $x^* < y^* < \tilde{z}^* < p^* < \tilde{t}^*$ hold; in 4 cases, the inequalities $\tilde{z}^* < x^* < y^* < p^* < \tilde{t}^*$ (for the interaction F−He at each of the four values of E) hold; in 2 cases, the inequalities $x^* < y^* < p^* < \tilde{z}^* < \tilde{t}^*$ hold; and in 1 case, the inequalities $p^* < x^* < y^* < \tilde{z}^* < \tilde{t}^*$ (for the interaction O−D_2 with $\Omega = 0$ at $E = -50$ meV) hold.

In all 177 cases examined, the ratio G_2 (eq 22) is greater than the ratio G_1 (eq 21), and as we saw, the inequalities $G_1 < 1 < G_2$ are valid in 47 cases. A comparison of the differences $u_k^{(1)} - u_k$ and $u_k^{(2)} - u_k^{(1)}$ is a more sensitive indicator of the applicability of the post-adiabatic analysis than a straightforward comparison of the nonadiabatic coupling matrix P and the first-order post-adiabatic coupling matrix Π_1 using the dimension correction of eq 14.

We have also considered another dimension correction for the elements z and t of the first-order post-adiabatic coupling matrix Π_1 (eq 13), namely,

$$\hat{z} = \text{hartree}^{1/2} z \qquad \hat{t} = \text{hartree}^{-1/2} t \tag{23}$$

However, such a correction usually yields a very large element $\hat{z}$ and a rather small element $\hat{t}$. The maximal values

$$\hat{z}^* = \max_R |\hat{z}(R)| = \text{hartree}^{1/2} \max_R |z(R)| \qquad \hat{t}^* = \max_R |\hat{t}(R)| = \text{hartree}^{-1/2} |t(R)|$$

of these elements satisfy the inequalities

$$\hat{t}^* < p^* < \hat{z}^*$$

in all 177 cases discussed above. Moreover, in *all* cases, $\hat{z}^*$ has been found to be larger (often more than an order of magnitude larger) than $\max\{\tilde{z}^*, \tilde{t}^*\}$.

However, if one considers the 42 two-state problems for which the first-order post-adiabatic potentials are real for all R at each of the 4 values of E and arranges those 4 values of $E = -50$, 25, 100, 200 meV in ascending order of the ratio

$$\frac{\hat{z}^*}{\max\{\tilde{z}^*, \tilde{t}^*\}}$$

then for 33 problems out of 42, one would obtain the sequence

$$200 \rightarrow 100 \rightarrow -50 \rightarrow 25 \text{ meV}$$

Moreover, this ratio is minimal at $E = 200$ meV for all 42 problems. If one arranges the values of E in ascending order of $\hat{z}^*$, one will obtain the sequence given by eq 20 (the higher E, the smaller $\hat{z}^*$) in all 42 problems. This suggests that the dimension correction of eq 23 could be useful at total energies higher than 200 meV.

In all 177 cases we discussed, all 10 functions x, y, z, t (and, consequently, $\hat{z}$ and $\hat{t}$, eq 23), $\tilde{z}$, $\tilde{t}$ (eq 14), δ_1, δ_2 (eq 16), Δ_1, and Δ_2 (eq 17) attain the maxima of their absolute values inside the interval $1.25 \le R \le 7$ Å and, as a rule, near the maximum of $|p|$, as expected. (See Figures 1−3 for an example.) Moreover, all 10 functions are small outside the interval of a strong enough nonadiabatic coupling. Thus, speaking of the relative magnitude of these functions, it does suffice to compare just the maxima of their absolute values, the approach utilized in the present paper.

V. Conclusions

As we saw in the previous section, even the first step of the post-adiabatic iteration scheme is an effective tool for reducing the coupling in many open-shell systems. However, the price for that is a more complicated structure of the coupling. The conventional nonadiabatic coupling in an n-state problem with the real Hamilton operator and a single slow variable is described by a skew-symmetric $n \times n$ matrix, whereas the post-adiabatic coupling of any order $s = 1, 2, \ldots$ is described by a Hamiltonian $2n \times 2n$ matrix. Therefore, an effective integration of multichannel stationary Schrödinger equations in the post-adiabatic representations would perhaps require the development of special methods. However, no new techniques are needed if one simulates the process under study on a collection of potentials and does not take the coupling into account (the decoupling approximation). As we already pointed out in the Introduction, using the first-order post-adiabatic potentials within such an approach may result in a better agreement with the experiment than using the usual adiabatic potentials. The examples are the scattering of an electron on a H atom[8−10] and the interaction between a Rydberg electron and an ionic core.[11,12]

It would be interesting to carry out the post-adiabatic analysis of the interactions of the Br, I, Se, and Te atoms with closed-shell particles. For these systems, one expects much smaller post-adiabatic couplings than for the respective interactions of the F, Cl, O, and S atoms because of the much larger fine-splitting constants of the open-shell partners.[68] The corresponding adiabatic potentials and nonadiabatic coupling matrix elements are exemplified by ab initio functions for the Br−He interaction.[61]

From a theoretical viewpoint, the most intriguing question of the theory of the post-adiabatic Schrödinger equations probably concerns the determination of the order $s_{\min}$ of the post-adiabatic representation corresponding to the minimal coupling for the given value of the slow coordinate. In the case where the adiabatic potentials and the nonadiabatic coupling P are holomorphic and P varies slowly (i.e., depends on "slow distance" $\rho = \epsilon R$, $0 < \epsilon \ll 1$), the asymptotics of $s_{\min}$ are ${}^{c}/_{\epsilon}$ with a certain constant c.[27] Indeed, each step of the post-adiabatic iterative procedure in this case involves differentiation with respect to ρ and multiplication by ϵ (eq 9). Typically, the sth derivative of a holomorphic function grows like $s!$ as s increases or, to be more precise, like $c^{-s}s!$ for a certain constant $c > 0$.[28] Consequently, the magnitude of the post-adiabatic coupling of order s can be very roughly estimated in the case in question as $({}^{\epsilon}/_{c})^{s}s! \approx [{}^{\epsilon s}/_{ce}]^{s}$. (We neglect the factor $(2\pi s)^{1/2}$ in Stirling's equation for $s!$.) The minimum of the function $[{}^{\epsilon s}/_{ce}]^{s}$ is attained at $s = {}^{c}/_{\epsilon}$ and is equal to $e^{-c/\epsilon}$. Such exponentially small estimates are well known, for example, in averaging theory.[25,70]

Acknowledgment. We thank A. A. Buchachenko for sending us the Fortran codes generating ab initio potentials V_Σ and V_Π for rare-gas sulfides[57] and A. I. Neishtadt for fruitful discussions on the post-adiabatic analysis. M.B.S. gratefully acknowledges the support received from the Italian Ministry of Foreign Affairs via a fellowship organized by the Landau Network-Centro Volta.

Appendix A. On the Nonexistence of Post-Adiabatic Representations with Several Slow Variables

As was already emphasized in the Introduction, one can construct post-adiabatic representations of multichannel stationary Schrödinger equations only for systems with a single slow degree of freedom. The physical consequences of this restriction were discussed in detail in our previous paper,[5] and here we explain why in the case of $N \geq 2$ slow coordinates even the first-order post-adiabatic potential energy surfaces cannot be defined.

The adiabatic n-channel stationary Schrödinger equation in the case of N slow variables $R_1, \ldots, R_N$ has the form[2,3,6,7]

$$-\sum_{\alpha=1}^{N}\frac{\hbar^2}{2\mu_\alpha}\left(I\frac{\partial}{\partial R_\alpha} + P_\alpha\right)^2\Phi + U\Phi = E\Phi \qquad (24)$$

where $\Phi(R) = \Phi(R_1, \ldots, R_N)$, $U(R)$, E, and I have the same meaning as for the $N = 1$ (eq 2) case, $P_1(R), \ldots, P_N(R)$ are the skew-Hermitian $n \times n$ matrices of the nonadiabatic couplings, and $\mu_1, \ldots, \mu_N$ are the reduced masses corresponding to coordinates $R_1, \ldots, R_N$. Let the matrices $P_1(R), \ldots, P_N(R)$ be real and skew-symmetric.

Introduce the notation

$$m_\alpha = \frac{\hbar}{(2\mu_\alpha)^{1/2}} \qquad 1 \leq \alpha \leq N$$

(cf. eq 4). Now eq 24 can be rewritten as

$$(\mathbf{D} + \mathbf{K}_0)\begin{pmatrix}\Phi \\ \Xi^{[1]} \\ \vdots \\ \Xi^{[N]}\end{pmatrix} = 0$$

where **D** is the operator

$$\mathbf{D} = \begin{pmatrix} m_1 I\partial/\partial R_1 & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ m_N I\partial/\partial R_N & 0 & \cdots & 0 \\ 0 & m_1 I\partial/\partial R_1 & \cdots & m_N I\partial/\partial R_N \end{pmatrix}$$

$\mathbf{K}_0$ is the $(N + 1)n \times (N + 1)n$ matrix

$$\mathbf{K_0} = \begin{pmatrix} m_1P_1 & I & 0 & \cdots & 0 & 0 \\ m_2P_2 & 0 & I & \cdots & 0 & 0 \\ \vdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ m_NP_N & 0 & 0 & \cdots & 0 & I \\ U - EI & m_1P_1 & m_2P_2 & \cdots & m_{N-1}P_{N-1} & m_NP_N \end{pmatrix} \qquad (25)$$

and

$$\Xi^{[\alpha]} = -m_\alpha\left(\frac{\partial\Phi}{\partial R_\alpha} + P_\alpha\Phi\right) \qquad 1 \leq \alpha \leq N$$

(cf. eq 5). In fact, **D** is the analogue of the operator $m(\mathrm{d}/\mathrm{d}R)$ in eq 3, and $\boldsymbol{K}_0$ is the analogue of the matrix

$$K_0 = \begin{pmatrix} 0 & I \\ U - EI & 0 \end{pmatrix} + m\begin{pmatrix} P & 0 \\ 0 & P \end{pmatrix}$$

in eq 3.

It is not hard to verify that the spectrum of the $(N + 1)n \times (N + 1)n$ matrix

$$\mathbf{Q_0} = \begin{pmatrix} 0 & I & 0 & \cdots & 0 & 0 \\ 0 & 0 & I & \cdots & 0 & 0 \\ \vdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & 0 & I \\ U - EI & 0 & 0 & \cdots & 0 & 0 \end{pmatrix}$$

is always the collection of all of the $(N + 1)$-th complex roots of n numbers $u_1 - E, \ldots, u_n - E$. (Recall that $u_1, \ldots, u_n$ are the diagonal entries of the diagonal matrix U.)

One would be able to include the nonadiabatic coupling matrices P_α in the adiabatic potentials u_k and obtain new (first-order post-adiabatic) potentials $u_k^{(1)}$ if the spectrum of the matrix $\mathbf{K}_0$ (eq 25) were the collection of all of the $(N + 1)$-th complex roots of certain numbers $\zeta_1, \ldots, \zeta_n$ for any diagonal $n \times n$ matrix U and any skew-symmetric $n \times n$ matrices $P_1, \ldots, P_N$. In this case, the potentials $u_1^{(1)}, \ldots, u_n^{(1)}$ would be just the numbers $\zeta_1 + E, \ldots, \zeta_n + E$. For $N = 1$, the spectrum of $\mathbf{K}_0$ is indeed the collection of all of the $(N + 1)$-th complex roots of some numbers $\zeta_1, \ldots, \zeta_n$ because for $N = 1$ the matrix $\mathbf{K}_0$ is Hamiltonian and its spectrum therefore has the form $\pm\lambda_1, \ldots, \pm\lambda_n$,[16−18] so one can set $\zeta_k = \lambda_k^2$ $(1 \le k \le n)$. But this is no longer true for $N \ge 2$ (provided that, of course, $n \ge 2$).

For instance, let $N = n = 2$ and $U = EI$,

$$P_1 = \begin{pmatrix} 0 & p_1 \\ -p_1 & 0 \end{pmatrix} \qquad P_2 = 0$$

where $p_1 \neq 0$. Then the 6×6 matrix $\mathbf{K}_0$ is

$$\mathbf{K}_0 = \begin{pmatrix} 0 & m_1p_1 & 1 & 0 & 0 & 0 \\ -m_1p_1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & m_1p_1 & 0 & 0 \\ 0 & 0 & -m_1p_1 & 0 & 0 & 0 \end{pmatrix}$$

It is easy to see that the eigenvalues of this matrix are

$$\pm \mathrm{i} m_1 p_1 \qquad (\pm 1 \pm \mathrm{i})\left(\frac{m_1 p_1}{2}\right)^{1/2}$$

(the square roots of $-m_1^2 p_1^2$ and the fourth roots of $-m_1^2 p_1^2$) and have the form

$$\lambda_1, \quad \frac{1}{2}(-1 \pm \mathrm{i}3^{1/2})\lambda_1, \quad \lambda_2, \quad \frac{1}{2}(-1 \pm \mathrm{i}3^{1/2})\lambda_2$$

(the cubic roots of λ_1^3 and λ_2^3) for no complex λ_1 and λ_2.

References and Notes

(1) Born, M.; Oppenheimer, R. *Ann. Phys.* **1927**, *84*, 457−484.

(2) Smith, F. T. *Phys. Rev.* **1969**, *179*, 111−123. Baer, M. *Chem. Phys. Lett.* **1975**, *35*, 112−118. Baer, M. *Chem. Phys.* **1976**, *15*, 49−57. Baer, M. *Mol. Phys.* **1980**, *40*, 1011−1013. Delos, J. B.; Thorson, W. R. *J. Chem. Phys.* **1979**, *70*, 1774−1790.

(3) Aquilanti, V.; Grossi, G.; Laganà, A. *Chem. Phys. Lett.* **1982**, *93*, 174−178.

(4) Aquilanti, V.; Cavalli, S.; Sevryuk, M. B. *J. Math. Phys.* **1994**, *35*, 536−559.

(5) Aquilanti, V.; Cavalli, S.; Rusin, L. Yu.; Sevryuk, M. B. *Theor. Chim. Acta* **1995**, *90*, 225−256.

(6) Baer, M. *Phys. Rep.* **2002**, *358*, 75−142 and references therein. Baer, M. *Adv. Chem. Phys.* **2002**, *124*, 39−142 and references therein. Kuppermann, A.; Abrol, R. *Adv. Chem. Phys.* **2002**, *124*, 283−322 and references therein.

(7) Adhikari, S.; Billing, G. D. *Adv. Chem. Phys.* **2002**, *124*, 143−196 and references therein.

(8) Klar, H.; Fano, U. *Phys. Rev. Lett.* **1976**, *37*, 1132−1134.

(9) Klar, H. *Phys. Rev. A* **1977**, *15*, 1452−1458.

(10) Klar, H.; Klar, M. *Phys. Rev. A* **1978**, *17*, 1007−1010.

(11) Clark, W.; Greene, C. H.; Miecznik, G. *Phys. Rev. A* **1996**, *53*, 2248−2261.

(12) Clark, W.; Greene, C. H. *Rev. Mod. Phys.* **1999**, *71*, 821−833.

(13) Rusin, L. Yu.; Sevryuk, M. B. *Proceedings of the Symposium in Memory of Professor Gert Due Billing*; Copenhagen, 2003.

(14) Holland, H. D. *The Chemistry of the Atmosphere and Oceans*; Wiley-Interscience: New York, 1978. Wayne, R. P. *Chemistry of Atmospheres: An Introduction to the Chemistry of the Atmospheres of Earth, the Planets, and Their Satellites*, 3rd ed.; Oxford University Press: Oxford, U.K., 2000.

(15) Aquilanti, V.; Cavalli, S.; Rusin, L. Yu.; Sevryuk, M. B. *Proceedings of the XVIII International Conference on Molecular Energy Transfer (COMET XVIII)*; San Lorenzo de El Escorial, Spain, 2003; p 38 (8-TH).

(16) Williamson, J. *Am. J. Math.* **1936**, *58*, 141−163.

(17) Arnold, V. I. *Mathematical Methods of Classical Mechanics*, 2nd ed.; Springer: New York, 1997.

(18) Bruno, A. D. *The Restricted Three-Body Problem: Plane Periodic Orbits*; Walter de Gruyter: Berlin, 1994.

(19) Yarkony, D. R. *J. Phys. Chem.* **1996**, *100*, 17439−17445.

(20) Alexander, M. H.; Manolopoulos, D. E.; Werner, H.-J. *J. Chem. Phys.* **2000**, *113*, 11084−11100.

(21) Arnold, V. I. *Sel. Math. (N. S.)* **1995**, *1*, 1−19.

(22) Chirkov, A. G. *Tech. Phys. Lett.* **2001**, *27*, 93−96.

(23) Born, M. *The Mechanics of the Atom*; Frederick Ungar Publishing Co.: New York, 1960.

(24) Bakai, A. S.; Stepanovskii, Yu. P. *Adiabatic Invariants*; Naukova Dumka: Kiev, 1981 (in Russian). Reinhardt, W. P. *Prog. Theor. Phys. Suppl.* **1994**, *116*, 179−205.

(25) Arnold, V. I.; Kozlov, V. V.; Neishtadt, A. I. *Mathematical Aspects of Classical and Celestial Mechanics*, 2nd ed.; Springer: Berlin, 1997.

(26) Wasow, W. *Linear Turning Point Theory*; Springer: New York, 1985.

(27) Neishtadt, A. I. Private communication, 2003.

(28) Krantz, S. G.; Parks, H. R. *A Primer of Real Analytic Functions*; Birkhäuser: Basel, Switzerland, 1992.

(29) Cater, F. S. *Real Analysis Exchange* **2001/2002**, *27*, 77−79.

(30) Kendrick, B. K.; Mead, C. A.; Truhlar, D. G. *Chem. Phys.* **2002**, *277*, 31−41.

(31) Neuhauser, D.; Baer, M.; Judson, R. S.; Kouri, D. J. *Comput. Phys. Commun.* **1991**, *63*, 460−481 and references therein. Billing, G. D.; Mikkelsen, K. V. *Advanced Molecular Dynamics and Chemical Kinetics*; Wiley-Interscience: New York, 1997 and references therein. Ge, J.-Y.; Zhang, J. Z. H. *J. Chem. Phys.* **1998**, *108*, 1429−1433.

(32) Nikitin, E. E.; Troe, J.; Ushakov, V. G. *J. Chem. Phys.* **1995**, *102*, 4101−4111.

(33) Zhu, Ch.; Nikitin, E. E.; Nakamura, H. *J. Chem. Phys.* **1996**, *104*, 7059−7067.

(34) Berry, M. V.; Robbins, J. M. *Proc. R. Soc. London, Ser. A* **1993**, *442*, 659−672.

(35) Berry, M. V. *Proc. R. Soc. London, Ser. A* **1996**, *452*, 1207−1220.

(36) Berry, M. V.; Sinclair, E. C. *J. Phys. A: Math. Gen.* **1997**, *30*, 2853−2861.

(37) Baer, M.; Englman, R. *Chem. Phys. Lett.* **1997**, *265*, 105−108. Baer, M. *J. Chem. Phys.* **1997**, *107*, 10662−10666.

(38) Baer, M.; Lin, Sh. H.; Alijah, A.; Adhikari, S.; Billing, G. D. *Phys. Rev. A* **2000**, *62*, 032506. Adhikari, S.; Billing, G. D.; Alijah, A.; Lin, Sh. H.; Baer, M. *Phys. Rev. A* **2000**, *62*, 032507.

(39) Tolstikhin, O. I.; Nakamura, H. *J. Chem. Phys.* **1998**, *108*, 8899−8921.

(40) Aquilanti, V.; Capecchi, G.; Cavalli, S. *Adv. Quantum Chem.* **2000**, *36*, 341−363.

(41) Aquilanti, V.; Candori, R.; Pirani, F. *J. Chem. Phys.* **1988**, *89*, 6157−6164.

(42) Aquilanti, V.; Luzzatti, E.; Pirani, F.; Volpi, G. G. *J. Chem. Phys.* **1988**, *89*, 6165−6175.

(43) Aquilanti, V.; Candori, R.; Mariani, L.; Pirani, F.; Liuti, G. *J. Phys. Chem.* **1989**, *93*, 130−135.

(44) Aquilanti, V.; Liuti, G.; Pirani, F.; Vecchiocattivi, F. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 955−964 and references therein.

(45) Aquilanti, V.; Candori, R.; Cappelletti, D.; Luzzatti, E.; Pirani, F. *Chem. Phys.* **1990**, *145*, 293−305.

(46) Aquilanti, V.; Cappelletti, D.; Pirani, F.; Rusin, L. Yu.; Sevryuk, M. B.; Toennies, J. P. *J. Phys. Chem.* **1991**, *95*, 8248−8255.

(47) Aquilanti, V.; Cappelletti, D.; Lorent, V.; Luzzatti, E.; Pirani, F. *Chem. Phys. Lett.* **1992**, *192*, 153−160.

(48) Aquilanti, V.; Cappelletti, D.; Lorent, V.; Luzzatti, E.; Pirani, F. *J. Phys. Chem.* **1993**, *97*, 2063−2071.

(49) Aquilanti, V.; Cappelletti, D.; Pirani, F. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1467−1474.

(50) Yamanishi, M.; Hirao, K.; Yamashita, K. *J. Chem. Phys.* **1998**, *108*, 1514−1521.

(51) Burcl, R.; Krems, R. V.; Buchachenko, A. A.; Szczęśniak, M. M.; Chałasiński, G.; Cybulski, S. M. *J. Chem. Phys.* **1998**, *109*, 2144−2154.

(52) Aquilanti, V.; Ascenzi, D.; Braca, E.; Cappelletti, D.; Pirani, F. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4081−4088.

(53) Hoffman, G. J.; Colletto, M. *J. Chem. Phys.* **2001**, *114*, 2219−2227.

(54) Buchachenko, A. A.; Krems, R. V.; Szczęśniak, M. M.; Xiao, Y.-D.; Viehland, L. A.; Chałasiński, G. *J. Chem. Phys.* **2001**, *114*, 9919−9928.

(55) Takayanagi, T.; Wada, A. *J. Chem. Phys.* **2001**, *115*, 6385−6393.

(56) Krems, R. V.; Buchachenko, A. A.; Szczęśniak, M. M.; Kłos, J.; Chałasiński, G. *J. Chem. Phys.* **2002**, *116*, 1457−1467.

(57) Kłos, J.; Chałasiński, G.; Krems, R. V.; Buchachenko, A. A.; Aquilanti, V.; Pirani, F.; Cappelletti, D. *J. Chem. Phys.* **2002**, *116*, 9269−9280.

(58) Aquilanti, V.; Grossi, G. *J. Chem. Phys.* **1980**, *73*, 1165−1172.

(59) Aquilanti, V.; Casavecchia, P.; Grossi, G.; Laganà, A. *J. Chem. Phys.* **1980**, *73*, 1173−1180.

(60) Aquilanti, V.; Luzzatti, E.; Pirani, F.; Volpi, G. G. *J. Chem. Phys.* **1980**, *73*, 1181−1186.

(61) De Lara-Castells, M. P.; Krems, R. V.; Buchachenko, A. A.; Delgado-Barrio, G.; Villarreal, P. *J. Chem. Phys.* **2001**, *115*, 10438−10449.

(62) Partridge, H.; Stallcop, J. R.; Levin, E. *J. Chem. Phys.* **2001**, *115*, 6471−6488.

(63) Aquilanti, V.; Cavalli, S.; Grossi, G. *Z. Phys. D* **1996**, *36*, 215−219.

(64) Aquilanti, V.; Ascenzi, D.; Braca, E.; Cappelletti, D.; Pirani, F. *Int. J. Mass Spectrosc.* **1998**, *179/180*, 67−76.

(65) Aquilanti, V.; Cavalli, S.; Pirani, F.; Volpi, A.; Cappelletti, D. *J. Phys. Chem. A* **2001**, *105*, 2401−2409.

(66) Aquilanti, V.; Cavalli, S.; De Fazio, D.; Volpi, A.; Aguilar, A.; Giménez, X.; Lucas, J. M. *Phys. Chem. Chem. Phys.* **2002**, *4*, 401−415.

(67) Kłos, J.; Chałasiński, G.; Szczęśniak, M. M. *Int. J. Quantum Chem.* **2002**, *90*, 1038−1048. Zeimen, W. B.; Kłos, J.; Groenenboom, G. C.; van der Avoird, A. *J. Chem. Phys.* **2003**, *118*, 7340−7352.

(68) Radzig, A. A.; Smirnov, B. M. *Reference Data on Atoms, Molecules, and Ions*; Springer: Berlin, 1985.

(69) Cramér, H. *Mathematical Methods of Statistics*, 2nd ed.; Princeton University Press: Princeton, NJ, 1999.

(70) Neishtadt, A. I. *J. Appl. Math. Mech.* **1984**, *48*, 133−139.