

Crossings of potential-energy surfaces in a magnetic field

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We investigate the interaction of molecular electronic states through nuclear motion in the presence of a homogeneous magnetic field. The different possibilities and effects of this interaction are classified according to the symmetries and the qualitative behavior of the diabatic energy curves. As a central result we show that conical intersections of electronic energy potential surfaces, which are in the field-free case common for polyatomic molecules, appear in the presence of a magnetic field already on the level of a diatomic molecule.

I. INTRODUCTION

The behavior of molecules in strong magnetic fields has become in the past ten years a subject of increasing interest. This interest was partly motivated by the astrophysical discovery of strong magnetic fields on white dwarfs and neutron stars. Most of the theoretical investigations on molecules in homogeneous external magnetic fields dealt with the H_2^+ ion.¹⁻⁴ The electronic ground state and first few excited states of the magnetically dressed H_2^+ system are now known to a relatively high accuracy.^{3,4} They were calculated for a relatively wide range of magnetic field strengths, covering the weak ($< 10^5$ T), intermediate, and strong ($> 10^6$ T) field regime, and for arbitrary orientations of the internuclear axis with respect to the magnetic field. There exist only a few investigations on many electron molecules.⁵ Detailed studies of the electronic potential surfaces are not only necessary for the calculation of the bound-state properties but also for the investigation of scattering processes in the presence of a magnetic field.

Molecular systems in magnetic fields exhibit many interesting new phenomena. In comparison with the field-free case there is an overall increase in binding energy which is mainly caused by the strong localization of the electrons near the nuclei. The bond lengths are contracted because of the more complete screening of the nuclei by the electronic clouds. As a consequence the minima of the electronic potential surfaces become more pronounced. The symmetry of, for example, the H_2^+ system in a magnetic field depends strongly on the orientation of the internuclear axis relative to the magnetic field. Certain configurations represent a minimum of the electronic potential energy and are therefore distinct. For the ground state of, for example, the H_2^+ ion it is well known¹⁻⁴ that the equilibrium position is given by the internuclear axis parallel to the magnetic field. Another interesting new phenomenon is the fact that certain in the field-free case unbound states (cf. $1\sigma_u$ H_2^+) become bound above some critical field strength.

From the abovementioned it is obvious that nuclear dynamics also experiences severe alterations in the pres-

ence of a magnetic field. One of the two rotational degrees of freedom of a diatomic molecule acquires vibrational character with increasing magnetic field strength. The potential barrier, which is a function of the angle of the magnetic field axis with the internuclear axis, prevents the molecule from free rotation. This effect is in the literature well known as the so-called hindered rotation.¹⁻³ Furthermore, there exists a field-strength-dependent rotation-vibration coupling which becomes important in the strong-field regime.

The subject of the present paper is the interaction of adjacent electronic states through the nuclear motion in the presence of a magnetic field. As in the field-free case we shall call this interaction vibronic interaction. There exist many phenomena like, for example, the radiationless decay of excited electronic states, predissociation, or certain chemical reaction mechanisms which are intimately related to the violation of the Born-Oppenheimer approximation as caused by vibronic interactions. We first briefly sketch some aspects of vibronic interactions in the field-free case. A necessary condition for the occurrence of vibronic interactions in molecules is that two or more electronic states come energetically close to each other. Usually this happens only for certain values of the nuclear coordinates. Neumann and Wigner have shown very early⁶ that in general, three parameters are necessary to bring together two eigenvalues of a Hermitian matrix. If the matrix is real symmetric only two parameters are sufficient. Of course the states under consideration should not differ in some essential properties like, for example, symmetry.

In the case of a diatomic molecule we have only one vibrational degree of freedom and therefore the noncrossing rule follows.^{6,7} However, already for a two-mode system two states may become exactly degenerate at a certain point of the nuclear coordinate space, forming a so-called conical intersection.⁸⁻¹⁰ A conical intersection necessarily causes a complete breakdown of the Born-Oppenheimer approximation.¹⁰ The majority of the theoretical studies of the vibronic coupling problem dealt with the following two cases: (i) the vibronic coupling of the components of a degenerate electronic state via a single degenerate vibrational mode (Jahn-Teller¹¹ and

Renner-Teller¹² effects) and (ii) the vibronic coupling of two nondegenerate electronic states of differential spatial symmetry via a single nontotally symmetric mode.

In the present paper we study, among other things, the vibronic coupling problem in the presence of a magnetic field and concentrate on diatomic molecules. Since the symmetry is lowered by the presence of the field, we discuss in Sec. II the symmetry groups for molecules in a homogeneous magnetic field. In Sec. III we investigate the behavior of the diabatic potential-energy surfaces as a function of the angle between the magnetic field axis and the internuclear axis. In Sec. IV we use the results of Secs. II and III in order to classify the different possibilities and effects of vibronic interactions between the diabatic states of a homonuclear diatomic molecule. Characteristic phenomena of vibronic coupling of *polyatomic* molecules in the absence of a magnetic field are shown to appear in the presence of a magnetic field already on the level of a *diatomic* molecule.

II. SYMMETRY CONSIDERATIONS FOR MOLECULES IN A MAGNETIC FIELD

In the presence of a magnetic field we have for a *diatomic* molecule already two vibrational degrees of freedom: the internuclear distance, and in addition, the angle between the internuclear axis and magnetic field axis. The electronic potential-energy surfaces are functions of these two parameters. Since the Hamiltonian of a molecule in a magnetic field is complex, these two parameters are, in general, not sufficient to achieve an intersection of two electronic potential surfaces. Only if we would include a third parameter by, for example, an additional arbitrarily oriented electric field would an intersection of two potential energy surfaces be possible. In spite of all that, vibronic coupling at intersections appears in the presence of a magnetic field already on the level of a diatomic molecule: two electronic states of *different* spatial symmetry are not subject to the noncrossing rule and might be coupled through the symmetry breaking vibrational mode associated with the angle between the internuclear axis and magnetic field axis. Before we discuss the topology of level crossings and vibronic interactions for diatomic molecules in a magnetic field we have to investigate the symmetry groups for molecules in a homogeneous magnetic field.

Our starting point for an investigation of the symmetry properties of the molecule is the electronic Hamiltonian of the system. This Hamiltonian can be obtained from the total molecular Hamiltonian by assuming infinitely heavy, fixed nuclei. For a more systematic derivation of the electronic Hamiltonian and an investigation of the Born-Oppenheimer approximation in the presence of a magnetic field we refer the reader to Refs. 13 and 14. In the following we assume the validity of the Born-Oppenheimer approximation for energetically well-separated states and we neglect all effects due to the center of mass motion of the molecule.^{14,15} In order to specify the electronic Hamiltonian we choose the symmetric gauge for the vector potential and the midpoint of the internuclear line as the coordinate origin. Our *z* axis

coincides with the internuclear axis and the magnetic field vector is chosen to be perpendicular to the *y* axis (cf. Fig. 1). θ denotes the angle between the field vector and the *z* axis. The Hamiltonian in atomic units then reads as follows:

$$\mathcal{H} = -\frac{1}{2} \sum_i \nabla_i^2 + \frac{1}{2} B \sum_i [(\sin\theta)l_{ix} + (\cos\theta)l_{iz}] + \frac{1}{8} B^2 \sum_i \{x_i^2 + y_i^2 + (\sin^2\theta)(z_i^2 - x_i^2) - [\sin(2\theta)]x_i z_i\} + V, \quad (2.1)$$

where the index *i* labels the electrons, *B* is the magnetic field strength, l_{ix} , and l_{iz} denote the corresponding components of the angular momentum of the *i*th electron and *V* contains all the Coulomb interaction terms. The trivial spin terms have been omitted. The second and third term of the Hamiltonian (2.1) represent the paramagnetic ($\propto B$) and diamagnetic ($\propto B^2$) contribution to the energy. From Eq. (2.1) it is obvious that the symmetry properties of the electronic Hamiltonian strongly depend on the angle θ .

It is not necessary to consider the dependence of the Hamiltonian (2.1) on the angle θ over the whole range $-\pi \leq \theta \leq \pi$. The Hamiltonian is invariant under each of the operations $(x_i, y_i, \theta) \rightarrow (-x_i, -y_i, -\theta)$ and $(x_i, \theta) \rightarrow (-x_i, \pi - \theta)$. As a consequence the electronic energies have the symmetry properties $E(\theta) = E(-\theta)$ and $E(\theta) = E(\pi - \theta)$. We can, therefore, restrict our investigations to the case where $0 \leq \theta \leq \pi/2$. Note that these symmetry properties apply to homonuclear as well as to heteronuclear diatomic molecules.

Let us first consider the case of a homonuclear diatomic molecule at $\theta = 0$, i.e., parallel internuclear axis and magnetic field vector (cf. Fig. 1). The following opera-

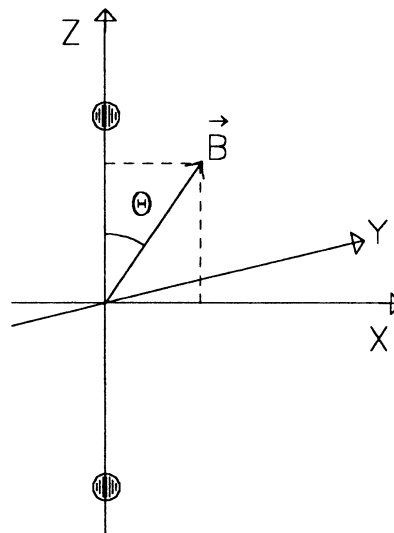


FIG. 1. Illustration of our coordinate system, magnetic field, and internuclear axis.

tions are symmetry operations of the Hamiltonian; i.e., the corresponding operators commute with the Hamiltonian (2.1) for $\theta=0$.

(i) Arbitrary rotations around the z axis. The angular momentum component $\sum_i l_{i_z}$ is a good quantum number, i.e., $[\mathcal{H}, \sum_i l_{i_z}] = 0$.

(ii) Inversion (parity P) of the electronic coordinates with respect to the midpoint of the internuclear axis, i.e., $[\mathcal{H}, P] = 0$.

(iii) Reflection of the electronic coordinates at the horizontal x - y plane (z parity).

The resulting symmetry group for a homonuclear diatomic molecule when the magnetic field is parallel to the internuclear axis is the $C_{\infty h}$ group. This symmetry group does not exist for molecules in the field-free case.¹⁶ It is an Abelian group which has only one-dimensional irreducible representations. With each complex irreducible representation the complex conjugate representation is also present. In the field-free case and for the finite analogue of the $C_{\infty h}$ group, i.e., for the C_{nh} group ($n \geq 3$), these two representations belong to degenerate states. This is due to the additional time-reversal symmetry of the Hamiltonian in the absence of a magnetic field. In the presence of a magnetic field we have no time reversal symmetry and degeneracies do not exist.

For arbitrary values of the angle θ parity is the only symmetry, i.e., the inversion group C_i is the molecular point group.

At $\theta=90^\circ$ we have the following symmetry operations.

(i) Rotations of 180° around the magnetic field axis.

(ii) Reflections of the electronic coordinates at the y - z plane (x parity).

The resulting symmetry group is the C_{2h} group.

For a heteronuclear diatomic molecule the symmetry operations and thus the symmetry point groups can be found analogously. The final results are for $0 \leq \theta \leq \pi/2$.

	Homo-nuclear	Hetero-nuclear
$\theta=0^\circ$	$C_{\infty h}$	C_∞
$\theta=90^\circ$	C_{2h}	C_s
θ arbitrary	C_i	C_1 (no symmetries exist)

We remark that the symmetry group is independent of the totally symmetric coordinate, i.e., the change of the internuclear distance, which is the same as in the field-free case.

For the determination of the symmetry groups of nonlinear polyatomic molecules both angles, which define the direction of the magnetic field axis, are of relevance. As a simple example we mention the H_2O molecule. In the free-field case it has the symmetry group C_{2v} . In the presence of a magnetic field there exist no symmetries, except the case that the magnetic field is oriented along

the C_2 axis of the field-free case. The corresponding residual symmetry group is the C_2 group.

III. TOPOLOGY OF POTENTIAL-ENERGY CURVES

In this section we give an overview of the simplest possible dependencies of the diabatic potential-energy curves on the angles θ . For simplicity we restrict our discussion to the case of a general diatomic molecule. The *diabatic* potential curves are smooth functions of the nuclear coordinates. If the potential energy curve in question is well separated from the other curves, it coincides with the adiabatic one which is the exact eigenvalue of the electronic Hamiltonian. The behavior of the energy curves in the vicinity of $\theta=0^\circ$ and $\theta=90^\circ$ is of special interest since these two positions are distinct by their higher symmetry. In order to investigate this behavior we use the Hellman-Feynman theorem which takes on the following appearance:

$$\frac{\partial E_\alpha}{\partial \theta} = \left\langle \Psi_\alpha \left| \frac{\partial \mathcal{H}}{\partial \theta} \right| \Psi_\alpha \right\rangle, \quad (3.1)$$

where Ψ_α is an eigenfunction of the electronic Hamiltonian \mathcal{H} with eigenvalue E_α . Equation (3.1) only makes sense for states which are smooth functions of θ and thus applies for all diabatic states. Using Eq. (2.1) and its symmetry properties discussed in Sec. II, we easily verify that the following relations hold:

$$\frac{\partial E_\alpha(\theta=0)}{\partial \theta} = \frac{\partial E_\alpha(\theta=\pi/2)}{\partial \theta} = 0. \quad (3.2)$$

The potential curves, therefore, exhibit extrema for the configurations where the internuclear axis is parallel and perpendicular to the magnetic field. The fact that the two positions $\theta=(0, \pi/2)$ are distinct, i.e., belong to higher symmetry, reflects itself in the dependency of the energy levels on the angle θ . It depends now on the second derivative whether the extremum under consideration is a maximum or a minimum. The corresponding formula for the second derivative reads as follows:

$$\begin{aligned} \frac{\partial^2 E_\alpha}{\partial \theta^2} = & \left\langle \Psi_\alpha \left| \frac{\partial^2 \mathcal{H}}{\partial \theta^2} \right| \Psi_\alpha \right\rangle + \left\langle \frac{\partial \Psi_\alpha}{\partial \theta} \left| \frac{\partial \mathcal{H}}{\partial \theta} \right| \Psi_\alpha \right\rangle \\ & + \left\langle \Psi_\alpha \left| \frac{\partial \mathcal{H}}{\partial \theta} \right| \frac{\partial \Psi_\alpha}{\partial \theta} \right\rangle. \end{aligned} \quad (3.3)$$

The derivative of the eigenfunction Ψ_α with respect to the angle θ can be obtained by first-order perturbation theory for small deviations from the reference configuration. The results for the two configurations $\theta=(0, \pi/2)$ are

$$\frac{\partial^2 E_\alpha(\theta=0)}{\partial \theta^2} = -\frac{1}{2} B M_\alpha + \frac{1}{4} B^2 \langle \Psi_\alpha(0) | Z^2 - X^2 | \Psi_\alpha(0) \rangle + 2 \sum_{\beta (\neq \alpha)} |V_{\alpha\beta}(0)|^2 / [E_\alpha(0) - E_\beta(0)], \quad (3.4a)$$

$$\begin{aligned} \frac{\partial^2 E_\alpha(\theta=\pi/2)}{\partial \theta^2} = & -\frac{1}{2} B \langle \Psi_\alpha(\pi/2) | L_x | \Psi_\alpha(\pi/2) \rangle - \frac{1}{4} B^2 \langle \Psi_\alpha(\pi/2) | Z^2 - X^2 | \Psi_\alpha(\pi/2) \rangle \\ & + 2 \sum_{\beta (\neq \alpha)} |V_{\alpha\beta}(\pi/2)|^2 / [E_\alpha(\pi/2) - E_\beta(\pi/2)], \end{aligned} \quad (3.4b)$$

with the following abbreviations:

$$Z^2 - X^2 = \sum_i [z_i^2 - x_i^2], \quad XZ = \sum_i x_i z_i, \quad L_x = \sum_i l_{ix} \quad (3.4c)$$

where M_α is the magnetic quantum number of the state $\Psi_\alpha(0)$, i.e., $L_z |\Psi_\alpha(0)\rangle = M_\alpha |\Psi_\alpha(0)\rangle$. The indices α, β label the eigenstates. The quantities $V_{\alpha\beta}(0), V_{\alpha\beta}(\pi/2)$ are special cases of the general matrix element

$$\begin{aligned} V_{\alpha\beta}(\theta) = & \frac{1}{2} B [(\cos\theta) \langle \Psi_\alpha | L_x | \Psi_\beta \rangle - (\sin\theta) \langle \Psi_\alpha | L_z | \Psi_\beta \rangle] \\ & + \frac{1}{8} B^2 \{ [\sin(2\theta)] \langle \Psi_\alpha | Z^2 - X^2 | \Psi_\beta \rangle \\ & - 2[\cos(2\theta)] \langle \Psi_\alpha | XZ | \Psi_\beta \rangle \}. \end{aligned} \quad (3.5)$$

From Eq. (3.4a) together with Eq. (3.5) we can draw the following conclusions. If the state $\Psi_\alpha(0)$ is energetically well separated from other electronic eigenstates $\Psi_\beta(0) (\beta \neq \alpha)$ we have only a small admixture of these states in the eigenfunction $\Psi_\alpha(\theta)$ for small angles θ . In this case the third term of Eq. (3.4a) can be neglected and the first and second terms determine the sign of the second derivative of the energy. For states with negative magnetic quantum number M_α we have for the whole range of the magnetic field strengths and for a wide range of internuclear distances a positive second derivative which implies a local minimum for the energy at $\theta=0^\circ$. Only for very small internuclear distances and/or positive magnetic quantum number M_α the extremum turns into a maximum. If the third term in Eq. (3.4a) is of relevance but not too large, i.e., perturbation theory is still applicable, it depends on the adjacent energy levels whether the contribution of this term to the second derivative is positive or negative. If α denotes the ground state we always have a negative contribution which might cause a maximum of the potential-energy curve at $\theta=0^\circ$. In case there exist energetically near-lying states $\Psi_\beta(0) (\beta \neq \alpha)$ the third term of Eq. (3.4a) can become large or even diverge (i.e., perturbation theory is not applicable). Vibronic interactions among the states can become important and play an essential role in determining the behavior of the energy curves. This case will be discussed extensively in Sec. IV.

If the magnetic field is perpendicular to the internuclear axis we can draw with the help of Eq. (3.4b) for an energetically well-separated state the following conclusions. For strong magnetic fields ($B > 1$ a.u.) and over a wide range of internuclear distances the second term in Eq. (3.4b) determines the sign of the second derivative to be negative. We, therefore, have a maximum of the energy at $\theta=90^\circ$. For intermediate field strengths and/or small internuclear distances it depends on the sign of the

expectation value of the x component of the total electronic angular momentum whether we obtain a minimum or maximum. For the case of other energetically near-lying states we again have the situation already mentioned above for $\theta=0^\circ$.

If vibronic interactions become important it is no more convenient to use a basis of adiabatic electronic states for the description of electronic and nuclear motion. Adiabatic electronic states are in the vicinity of avoided crossings or conical intersections strongly varying functions of the nuclear coordinates. The calculation of the solutions of the electronic Schrödinger equation as well as the evaluation of the corresponding nonadiabatic coupling elements become, therefore, considerably more complicated.

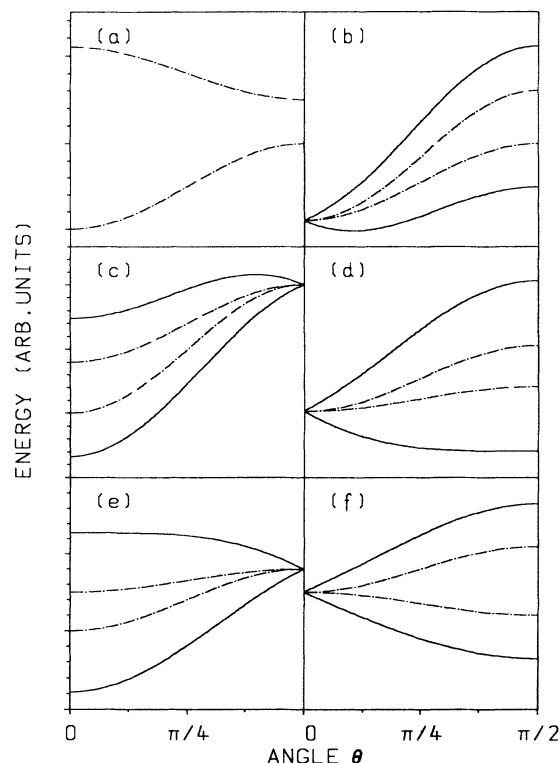


FIG. 2. Diabatic (dash-dotted lines) and adiabatic (solid lines) potential-energy curves as a function of the angle θ between the magnetic field and the internuclear axis. The energy scale is given in arbitrary units. (a) The different possibilities for the behavior of the diabatic energy curves are sketched. (b)–(f) The adiabatic energy curves together with their diabatic counterparts for the case of different symmetry of the adiabatic-diabatic electronic states at only one of the two distinct positions $\theta=0, \pi/2$.

As an alternative we will use diabatic states which are smooth and slowly varying functions of the nuclear coordinates. The vibronic interaction between the diabatic states is then contained in the off-diagonal coupling terms of the electronic matrix Hamiltonian.

In Fig. 2(a) we illustrate the simplest possible dependencies of the *diabatic* electronic energy curves on θ according to the results of our discussion. Either the energy curve exhibits a minimum at $\theta=0^\circ$ and a maximum at $\theta=90^\circ$ or vice versa. We remark that the observations made in Ref. 4 for the special case of the H_2^+ ion support the present results. The above considerations are indispensable for a discussion of vibronic interactions in the presence of a magnetic field, which is the main interest of this paper.

IV. VIBRONIC INTERACTIONS IN A MAGNETIC FIELD

In Sec. III we have shown that the most simple behavior of diabatic energy curves as a function of the angle θ is given by the two possibilities illustrated in Fig. 2(a). Let us now consider the case of two diabatic electronic states of a homonuclear diatomic molecule which come close in energy and interact. In the following we will give a survey of the static problem. According to the symmetry of the two interacting diabatic states and their energy behavior [cf. Fig. 2(a)] we will discuss the different possibilities of the behavior of the adiabatic energy curves and potential surfaces.

First of all we remind the reader of the fact that parity is a good quantum number for arbitrary angles θ . Diabatic states belonging to different parity, therefore, do not interact; i.e., they are allowed to cross without disturbing each other. Consequently, we will consider two states of the *same* parity. As already mentioned, the number of parameters is too small in order to achieve a crossing for the angle range $0^\circ < \theta < 90^\circ$, i.e., the noncrossing rule holds. Vibronic interactions in the range $0^\circ < \theta < 90^\circ$, therefore, appear only in the form of avoided crossings. Although these crossings can complicate considerably the behavior of the two-dimensional potential surfaces and might change their maximum-minimum properties; they are, in principle, nothing else but the two-dimensional generalization of the avoided crossings of diatomic in the absence of a magnetic field. If, in addition, the two states under consideration have the *same* symmetry at the distinct positions $\theta=0^\circ$ and $\theta=90^\circ$ we can expect as candidates for vibronic interactions *only* the above-mentioned avoided crossings. Therefore, we restrict our discussion to the more interesting and relevant situation, where the two interacting states belong to different spatial symmetry at least at one of the two distinct positions.

In the following we discuss basic cases out of which more complicated cases can be constructed by analogy. As a first case we study the situation of two diabatic states of different spatial symmetry at $\theta=0^\circ$ and equal symmetry at $\theta=90^\circ$. Furthermore we assume both states to have their minimum at $\theta=0^\circ$ and their maximum at $\theta=90^\circ$. Since the two states should have the same parity but differ in some spatial symmetry, we choose them to

belong to different z parity (reflection with respect to the x - y plane in Fig. 1). This choice is necessary, otherwise the coupling between the two states vanishes [see Eqs. (4.2) and (4.3) below]. In order to construct a simple model Hamiltonian for our two-state problem we must use a diabatic representation of our basis. The simplest way to do this is to choose two crude adiabatic electronic states ϕ_α, ϕ_β which are eigenfunctions of the electronic Hamiltonian (2.1) at fixed value of the internuclear distance and the angle θ . In our case ϕ_α, ϕ_β are energy eigenfunctions for the parallel internuclear and magnetic field axis. Our model Hamiltonian reads as follows:

$$\underline{H} = \begin{pmatrix} \langle \phi_\alpha | \mathcal{H} | \phi_\alpha \rangle & \langle \phi_\alpha | \mathcal{H} | \phi_\beta \rangle \\ \langle \phi_\beta | \mathcal{H} | \phi_\alpha \rangle & \langle \phi_\beta | \mathcal{H} | \phi_\beta \rangle \end{pmatrix}. \quad (4.1)$$

As already mentioned we have to deal with a two-mode problem; i.e., the matrix elements of the Hamiltonian (4.1) are functions of the totally symmetric mode, which is already present in the zero-field case, and the angle θ . In order to obtain the analytical behavior of the Hamiltonian (4.1) in the vicinity of $\theta=0^\circ$ and around some internuclear distance we expand its matrix elements in the following form:

$$\begin{aligned} \langle \phi_\gamma | \mathcal{H} | \phi_\gamma \rangle &\approx E_\gamma + \kappa_\gamma Q + (\omega_\gamma/2)Q^2 + \rho_\gamma \theta^2, \\ \langle \phi_\alpha | \mathcal{H} | \phi_\beta \rangle &\approx \sigma \theta, \end{aligned} \quad (4.2)$$

where E_γ is the energy eigenvalue of the eigenfunction ϕ_γ at $\theta=0^\circ$ and $Q=0$ (γ is α or β). Q is chosen dimensionless. The coefficients ρ_γ and σ can be obtained explicitly from the derivatives of the electronic Hamiltonian (2.1) with respect to the angle θ :

$$\begin{aligned} \rho_\gamma &= \frac{1}{8} B^2 \langle \phi_\gamma | Z^2 - X^2 | \phi_\gamma \rangle - \frac{1}{4} B M_\gamma, \\ \sigma &= \frac{1}{2} B \langle \phi_\alpha | L_x | \phi_\beta \rangle - \frac{1}{4} B^2 \langle \phi_\alpha | XZ | \phi_\beta \rangle. \end{aligned} \quad (4.3)$$

They contain a linear and quadratic term in the magnetic field strength. In addition they depend implicitly via the wave function ϕ_γ on the field strength. The coefficients $\kappa_\gamma, \omega_\gamma$ are given implicitly by the expectation values of the first and second derivative of the Hamiltonian (2.1) with respect to the totally symmetric mode Q . In Eq. (4.2) we have expanded the diagonal terms of the matrix (4.1) up to second order in the coordinates Q and θ . The off-diagonal terms have been expanded up to first order in Q and θ . In the off-diagonal element of the Hamiltonian the constant as well as the term linear in the totally symmetric coordinate Q vanish because of the different spatial symmetry (z parity) of the states ϕ_α and ϕ_β . The only remaining term is the one linear in the angle θ . We remark that a more complete expansion of the off-diagonal terms of the matrix Hamiltonian (4.1) would include an additional bilinear term which is proportional to the product of Q and θ . This term is not of relevance for our discussion below and has been omitted.

At this stage an expert for vibronic interactions immediately realizes that the Hamiltonian (4.1) together with Eq. (4.2) is the simplest possible model for vibronic interactions with a tuning mode Q and a non-totally-symmetric coupling mode θ similarly to that encountered

in the field-free case for polyatomic molecules.¹⁰ In order to gain some physical insight into our vibronic coupling problem we investigate the *adiabatic* electronic potential surfaces. The latter can be obtained by diagonalizing the electronic matrix Hamiltonian (4.1). They take on the following appearance:

$$W_{1,2} = \frac{(E_\alpha + E_\beta)/2 + [(\kappa_\alpha + \kappa_\beta)/2]Q}{2} + [(\omega_\alpha + \omega_\beta)/4]Q^2 + [(\rho_\alpha + \rho_\beta)/2]\theta^2 \mp \left\{ \frac{1}{4} \left[(E_\alpha - E_\beta) + (\kappa_\alpha - \kappa_\beta)Q + [(\omega_\alpha - \omega_\beta)/2]Q^2 + (\rho_\alpha - \rho_\beta)\theta^2 \right]^2 + |\sigma|^2\theta^2 \right\}^{1/2}. \quad (4.4)$$

So far we have not used the fact that a crossing of our two energy levels (diabatic or adiabatic) is possible at $\theta=0^\circ$ owing to their different spatial symmetry. We, therefore, expand our Hamiltonian (4.1) around the point of degeneracy in nuclear configuration space, i.e., $E_\alpha = E_\beta = E$ in Eq. (4.4). For simplicity we neglect the difference between the harmonic diabatic frequencies of the two states; i.e., we take $\omega_\alpha = \omega_\beta = \omega$ and $\rho_\alpha = \rho_\beta = \rho$. Our adiabatic potential surfaces finally read as follows:

$$W_{1,2} = E + [(\kappa_\alpha + \kappa_\beta)/2]Q + (\omega/2)Q^2 + \rho\theta^2 \mp \left[\frac{1}{4}(\kappa_\alpha - \kappa_\beta)^2 Q^2 + |\sigma|^2\theta^2 \right]^{1/2}. \quad (4.5)$$

In Fig. 3 we provide a two-dimensional plot of the two adiabatic potential surfaces W_1, W_2 plotted vs the internuclear elongation Q and the angle θ (in degrees). In addition we have sketched in Fig. 2(b) the dependence of the two diabatic and corresponding adiabatic energy levels on θ at $Q=0$ and for the whole range $0^\circ \leq \theta \leq 90^\circ$. Although Eq. (4.5) is only quantitatively correct in the vicinity of the conical

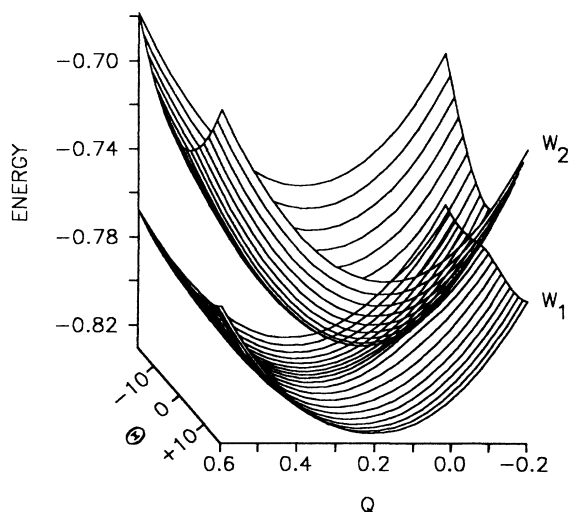


FIG. 3. The adiabatic potential energy surfaces W_1, W_2 are plotted vs the internuclear elongation Q and the angle θ (in degrees). The following set of parameter values has been used (in arbitrary units): $E = -0.8$, $\kappa_\alpha = -0.2$, $\kappa_\beta = -0.1$, $\omega = 0.8$, $|\sigma| = 2 \times 10^{-3}$, $\rho = 8.5 \times 10^{-5}$.

intersection, it correctly reflects the qualitative aspects of the surfaces for a larger range of coordinates. The two surfaces in Figs. 3 and 2(b) exhibit some characteristic properties of vibronic interaction. First we observe that there exists a single point where the upper surface touches the lower one. This point is well known as a so-called conical intersection point.⁸⁻¹⁰ Second, we can see a lowering of the symmetry of the equilibrium position of the lower surface. The lower surface has its minimum not at the position $\theta=0^\circ$ with $C_{\infty h}$ as a symmetry group but at some value $\theta \neq 0^\circ$ with parity as the only remaining symmetry. We encounter a local breaking of the molecular symmetry. The upper surface becomes steeper in comparison with its diabatic analogue. Both effects, symmetry lowering and enhanced steepness, are a consequence of the repulsion of the diabatic surfaces via the vibronic coupling. Furthermore we remark that the nonadiabatic coupling terms diverge at the conical intersection point which indicates the complete breakdown of the adiabatic approximation. For the case of near-degenerate surfaces we obtain a threshold behavior: Above some critical value of the coupling constant $|\sigma|$ the onset of the local symmetry breaking is observed. We conclude that conical intersections and the resulting phenomena appear in the presence of a magnetic field already on the level of a diatomic molecule. The angle θ between the internuclear and the magnetic field axis thereby plays the role of the "symmetry breaking coordinate."

We remark that a more elaborate discussion of the behavior of the energy potential surfaces over the whole range $0^\circ \leq \theta \leq 90^\circ$ is possible by, for example, using the following diabatic states:

$$\phi = c_1(\theta)\phi(0^\circ) + c_2(\theta)\phi(90^\circ),$$

where c_1 and c_2 are θ -dependent coefficients which determine the mixture of the crude adiabatic states $\phi(0^\circ)$ and $\phi(90^\circ)$ in the diabatic wave function ϕ .

Let us now return to our general discussion of two vibronically interacting diabatic states. So far we have discussed the case of two diabatic states with a minimum of the energy at $\theta=0^\circ$, different spatial symmetry at $\theta=0^\circ$, and the same symmetry at $\theta=90^\circ$. Furthermore we have assumed an exact degeneracy of the two levels at $\theta=0^\circ$. In Fig. 2(c) we have plotted the case of different symmetry at $\theta=90^\circ$ and the same symmetry at $\theta=0^\circ$. This case is realized if the two diabatic electronic states under consideration have different x parity at $\theta=90^\circ$. The degeneracy appears now at $\theta=90^\circ$. Hence it follows that the upper adiabatic level develops a *maximum* for an angle $\theta \neq 90^\circ$. The lower level simply becomes steeper because of the repulsion of the two diabatic levels.

A new qualitatively effect appears if we have a very strong vibronic coupling and/or a small variation of the energy of one of the diabatic levels from $\theta=0^\circ$ to $\theta=90^\circ$. The effect is illustrated in Fig. 2(d) where the two diabatic states have different symmetry at $\theta=0^\circ$, the same symmetry at $\theta=90^\circ$, and possess their minima at $\theta=0^\circ$. The lower adiabatic level develops a minimum [cf. Fig. 2(b)] which now, due to the strong coupling and/or the small energy difference, shifts to the angle $\theta=90^\circ$. The lower adiabatic curve has thus developed a minimum at $\theta=90^\circ$,

whereas its diabatic counterpart exhibits a maximum at $\theta=90^\circ$. We will call this effect of vibronic interactions the "adiabatic flipover." The upper adiabatic level becomes steeper but retains its maximum-minimum properties. Obviously the same effects is also possible if the two diabatic states have different symmetry at $\theta=90^\circ$. This case is illustrated in Fig. 2(e). The maximum of the upper adiabatic level [cf. Fig. 2(c)] now shifts to $\theta=0^\circ$ whereas the lower adiabatic level becomes steeper but still has the same maximum-minimum properties as its diabatic counterpart.

Another possibility for vibronic interactions of two diabatic levels can be obtained if we assume the two levels to have their minimum at $\theta=0^\circ$ and $\theta=90^\circ$, respectively. This case is illustrated in Fig. 2(f) for different symmetries of the diabatic states at $\theta=0^\circ$ and equal symmetry at $\theta=90^\circ$. Nothing exciting happens. The upper and lower adiabatic level simply become steeper but retain their maximum-minimum properties.

Finally, we have to discuss the case that the two diabatic states have different symmetry at $\theta=0^\circ$ as well as at $\theta=90^\circ$. Let us first assume that both diabatic levels have their minimum at $\theta=0^\circ$. If the energy difference of the two diabatic states is small at $\theta=90^\circ$ we obtain the adiabatic curves illustrated in Fig. 4(a). The upper adiabatic level develops a maximum at $\theta\neq 90^\circ$ and a minimum at $\theta=90^\circ$. The lower level exhibits the local symmetry breaking effect and shows a minimum at $\theta\neq 0^\circ$. With increasing energy difference between the diabatic states at $\theta=90^\circ$ the vibronic interaction at $\theta=90^\circ$ becomes negligible and we arrive at a qualitative behavior of the adiabatic energy curves similar to Fig. 2(b). In Fig. 4(b) we illustrate the case where the upper diabatic curve has its minimum at $\theta=0^\circ$ and the lower one at $\theta=90^\circ$. For a small energy difference at $\theta=90^\circ$ [cf. Fig. 4(b)] the upper adiabatic level obtains a maximum and the lower adiabatic level a minimum at $\theta\neq 90^\circ$. For large diabatic energy differences at $\theta=90^\circ$ vibronic interaction is negligible around $\theta=90^\circ$ and we arrive at a behavior of the adiabatic energy curves similar to that given in Fig. 2(f). Obviously it is also possible that only one of the two adiabatic

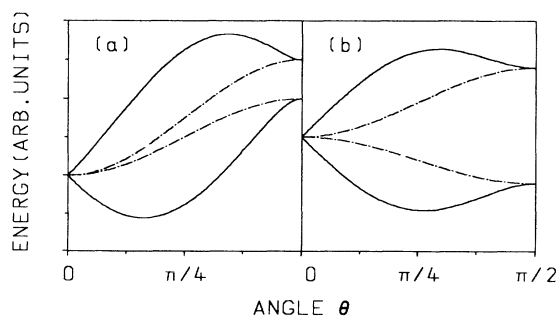


FIG. 4. Diabatic (dash-dotted lines) and adiabatic (solid lines) potential-energy curves as a function of the angle θ between the magnetic field and the internuclear axis. The adiabatic-diabatic electronic states under consideration possess different symmetry at $\theta=0$ as well as $\theta=\pi/2$.

levels develops an additional extremum in comparison with its diabatic counterpart.

The dependencies of the adiabatic energies on θ illustrated in Figs. 2 and 4 are the most simple ones. They can become much more complicated in case the diabatic states cross each other for $\theta=0^\circ$ and 90° . The adiabatic states will then exhibit additional avoided crossings. Finally we mention that possible candidates for vibronic interactions have been observed in numerical calculations of the adiabatic electronic energy surfaces of the H_2^+ ion in Ref. 4. The $1\pi_u - 1\sigma_u$ as well as the $1\pi_g - 1\delta_g$ crossing for $B=1$ are probable examples for the conical intersection of two adiabatic electronic potential surfaces.

V. SUMMARY AND CONCLUSIONS

Crossings of electronic potential-energy surfaces and the resulting vibronic interaction between them are of relevance for the bound-state properties of the underlying system and also for scattering processes and chemical reaction mechanisms. Such crossings of the projectile-target molecule potential surfaces enable the collision partner to change the surface it is moving on resulting in a gain or loss of kinetic energy of the projectile and target.

In order to obtain an overview of the static aspects of vibronic interaction in the presence of a strong magnetic field we have, as a first step, investigated the symmetry point groups for diatomic molecules in a homogeneous magnetic field. Two positions are distinct, i.e., possess higher symmetry: the configurations with parallel and orthogonal internuclear axis and magnetic field axis. The diabatic energies as a function of the angle θ between the magnetic field axis and the internuclear axis exhibit extrema at these two positions. Whether these extrema are minima or maxima depends, among other things, on the internuclear distance and the magnetic field strength. Taking account of the θ dependence of the diabatic energies and the symmetries of the corresponding diabatic states at $\theta=0^\circ$ and $\theta=90^\circ$ we discussed the different possibilities and effects of vibronic interaction. As a central result we observed that conical intersections appear in the presence of a magnetic field already for a diatomic molecule. The angle θ thereby plays the role of the "coupling mode." As a natural consequence we obtain effects like, for example, symmetry lowering, which are, in the absence of a magnetic field, common for polyatomic molecules only. A particular possible effect of vibronic interactions is the so-called adiabatic flipover in which the maximum and minimum of a potential curve are interchanged by vibronic interaction.

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