Treatment of Jahn-Teller and *pseudo*-Jahn-Teller effects

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1 Some historical notes

(With special regards to Z. L.)

The Jahn-Teller effect came into life shortly after the Big Bang, right when the first polyatomic molecules started to form, $\text{H}_3$ for instance. Unfortunately, there were no scientists around to witness this seminal event, at least non I would know of. Since we do not know the actual birth date, we cannot have a nice birthday party for the Jahn-Teller effect, otherwise we surely would have.

Strangely enough, it took more than 13 billion years for this effect to be discovered. The birth date of Edward Teller (Hungarian: Teller Ede) is known, actually it was Jan. 15, 1908 that he came into life in Budapest, but he did not discover the effect, named after him, right then. He first had to meet Lew Dawidowitsch Landau in 1934, who was born Jan. 22, 1908 in Baku. Landau claimed that the degeneracy of an electronic state, which is induced by symmetry, will in general be destroyed. Teller tried to argue against this statement, at least for linear molecules this rule should not apply.

Inspired by this discussion, he started to work on this problem together with his student Hermann Arthur Jahn (born May 31, 1907 in Colchester, Essex, died 1979 in Southampton). They studied the situation for all conceivable symmetries of molecules and found no exceptions from Landau’s theorem. The situation for linear molecules has been investigated before by R. Renner [R. Renner Z. Phys. 92 (1934) 172].

Theorem: … All non-linear nuclear configurations are therefore unstable for an orbitally degenerate electronic state.


We owe to Teller not only the early investigations on vibronic coupling problems, but also such nice things as nuclear weapons and the hydrogen bomb. It appears that he was a thoroughly nasty fellow, easily getting into conflicts with his colleagues. He was promoting nuclear warfare throughout his life, which in his later life seems to have been his main job. Therefore, he was awarded the Ig-Nobel prize “for his lifelong efforts to change the meaning of peace as we know it” in 1991 and the Presidential Medal of Freedom by President George W. Bush just about two months before his death on Sept. 9, 2003. In contrast, Lew Landau was awarded the Nobel prize in 1962 for his fundamental work on the theory of condensed matter (e. g. super fluidity). The same year he was involved in a bad car accident from which he never fully recovered till his death on April 1, 1968.
2 Symmetry: Abelian and non-Abelian point groups

For the definition of a group we need elements $a, b$ of a field and an operation $\circ$. Let's assume that $\mathbb{G}$ is a set with elements $a, b$ that fulfill

$$a, b \in \mathbb{G} \Rightarrow (a \circ b) \in \mathbb{G}.$$  \hspace{1cm} (closure)

The group $\mathbb{G}$ is \textit{closed} with respect to the operation $\circ$.

\begin{definition}
A group is a system $(\mathbb{G}, \circ)$ that consists of an operation $\circ$ with respect to which the set $\mathbb{G}$ is closed and which fulfills the following conditions:
\begin{enumerate}
\item $a \circ (b \circ c) = (a \circ b) \circ c \quad \forall \ a, b, c \in \mathbb{G}$ (associative).
\item It exits a \textit{neutral element} $e \in \mathbb{G}$ with $e \circ a = a$ \quad $\forall \ a \in \mathbb{G}$. \\
3. For each element $a \in \mathbb{G}$ there exists an \textit{inverse element} $a^{-1} \in \mathbb{G}$ with $a \circ a^{-1} = a^{-1} \circ a = e$.
\end{enumerate}
\end{definition}

\begin{definition}
A group is called Abelian if

$$a \circ b = b \circ a \quad \forall \ a, b \in \mathbb{G}$$

i. e. if elements $a, b$ commute with respect to $\circ$.
\end{definition}

\begin{corollary}
The symmetry operations $\hat{S}_k$ of any geometrical object, that transform this object into itself, form a group, the so-called \textit{point group}.
\end{corollary}

\begin{theorem}
The representation of any point group, containing a rotational axis $C_n$ with $n > 2$, contains at least one \textit{degenerate} irreducible representation. Thus, such a point group is \textit{non-Abelian}.
\end{theorem}

The symmetry plays an important role in the description of molecules. Every molecule has a certain symmetry corresponding to a point group. Letting any of the symmetry operators of the group act on the molecule must not have any effect on the physics of the system. Therefore, we can require that $[\hat{H}, \hat{S}] = 0$, where $\hat{H}$ is the Hamiltonian of the system. In fact, the existence of degenerate irreducible representations of non-Abelian point groups is reflected in degenerate (electronic) states for molecules of the respective symmetry.
Wolfgang Eisfeld

Treatment of Jahn-Teller and pseudo-Jahn-Teller effects

Table 1: Character table of the $D_{3h}$ point group

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$\sigma_h$</th>
<th>$2S_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A'_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A'_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$E'$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>$A''_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$A''_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$E''$</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

$\alpha_{xx} + \alpha_{yy}$, $\alpha_{zz}$

$\alpha_{xx} - \alpha_{yy}$, $\alpha_{xy}$

$\alpha_{xy}$, $\alpha_{zz}$

3 Adiabatic, crude adiabatic, and diabatic states

The coupled Schrödinger equation in the adiabatic representation reads

$$\left[\hat{T}_n 1 + \mathbf{V}(\mathbf{Q}) - E1\right] \chi(\mathbf{Q}) = \Lambda \chi(\mathbf{Q}). \quad (1)$$

$\hat{T}_n$ is the nuclear kinetic operator, $\mathbf{V}(\mathbf{Q})$ is a diagonal matrix, representing the adiabatic potential energy surfaces, $\chi(\mathbf{Q})$ is a vector containing the nuclear wave functions, and $\Lambda$ is the nonadiabatic coupling matrix. The matrix elements $\lambda_{ij}$ are expressed as

$$\lambda_{ij} = -\langle \phi_i | \hat{T}_n | \phi_j \rangle + \langle \phi_i | \nabla | \phi_j \rangle \nabla,$$  \quad (2)

where $\phi$ are the adiabatic electronic wave functions which are eigenfunctions of the electronic Hamiltonian

$$\hat{H}_e \phi_i(\mathbf{r}, \mathbf{Q}) = V_i(\mathbf{Q}) \phi_i(\mathbf{r}, \mathbf{Q}) \quad (3)$$

The full adiabatic molecular wave function can be expanded as

$$\Psi(\mathbf{r}, \mathbf{Q}) = \sum_i \phi_i(\mathbf{r}, \mathbf{Q}) \chi_i(\mathbf{Q}). \quad (4)$$

As we know, the $\lambda_{ij}$ diverge at a conical intersection which causes numerical problems. Therefore, we seek for a way to reformulate the problem such that this kind of behaviour is avoided. We first can re-write eq. (4) in vector form as $\Psi = \phi^\dagger \chi$. Then we introduce a unitary transformation $\mathbf{U}(\mathbf{Q})$ and insert this into eq. (4) which yields

$$\Psi(\mathbf{r}, \mathbf{Q}) = \phi^\dagger \mathbf{U} \chi = (\mathbf{U}^\dagger \phi )^\dagger \mathbf{U}^\dagger \chi = \phi^{(d)\dagger} \chi^{(d)}. \quad (5)$$

So far the transformation is not further specified but we want to simplify the coupled Schrödinger equation eq. (1). This can be achieved by the requirement $\nabla \mathbf{U} + \mathbf{F} \mathbf{U} = 0$ ($\mathbf{F}_{ji} = \langle \phi_j | \nabla | \phi_i \rangle$, $\{ \phi_k \}$ is a complete basis) and we get after some math

$$\left[ (\mathbf{V} - E1) \mathbf{U} - \frac{\hbar^2}{2m} \mathbf{U} \nabla^2 \right] \chi^{(d)} = 0. \quad (6)$$
We can multiply with $U^\dagger$ from the left and obtain the working equations in the diabatic basis

$$ \begin{bmatrix} V^{(d)} - E \mathbf{1} - \frac{\hbar^2}{2m} \nabla^2 \end{bmatrix} \chi^{(d)} = 0. \quad (7) $$

The nonadiabatic coupling is now accounted for by the diabatic potential matrix $V^{(d)} = U^\dagger V U$ in eq. (7), which is no longer diagonal. However, if the matrix elements $V^{(d)}_{ij}$ are free of pathological problems as is generally the case, eq. (7) can be solved by standard methods. The main issue is to find the appropriate adiabatic-to-diabatic transformation $U$.

In this respect, the **crude adiabatic approximation** may be helpful by which the full molecular wave function is expressed as

$$ \Psi(r, Q)^{\text{crude}} = \sum_i \phi_i^0(r, Q_0) \chi_i^0(Q). \quad (8) $$

In this truly crude approximation, the total wave function at any point $Q$ in coordinate space is expressed using the electronic wave functions $\phi_i^0$ at the reference point $Q_0$ [H. C. Longuet-Higgins, *Adv. Spectrosc.*, 2 (1961) 429]. It has been argued that the convergence of the expansion is terribly slow and this is certainly true. However, we hardly ever need to carry out this expansion and much rather express the potential functions $h_{ij}$ directly. Nevertheless, the crude adiabatic approximation is extremely useful for deriving Jahn-Teller and *pseudo*-Jahn-Teller Hamiltonians based on the symmetry properties of the $\phi_i^0$ at a highly symmetric reference point $Q_0$ as will be shown in the following.

## 4 Jahn-Teller and *pseudo*-Jahn-Teller Hamiltonians and their derivation

The Jahn-Teller effect is observed for systems which have degenerate electronic states and vibrational modes due to their symmetry. Let's assume for simplicity that we have only doubly degenerate $E$ states and $e$ modes.

The Jahn-Teller theorem states that **any nonlinear polyatomic system in a symmetry-induced degenerate state will distort such that the degeneracy is lifted**. Why is this the case? Let's have a look at the diabatic and adiabatic potential matrices that correspond to our two-state subspace. We know that in the adiabatic representation $V(Q)$ is diagonal and therefore

$$ \det \begin{pmatrix} V_{11}^{(d)} - V_1 & V_{12}^{(d)} \\ V_{12}^{(d)} & V_{22}^{(d)} - V_2 \end{pmatrix} \equiv 0. \quad (9) $$

The solution for the adiabatic potentials is

$$ V_{1/2} = \frac{1}{2} \left[ (V_{11}^{(d)} + V_{22}^{(d)}) \pm \sqrt{(V_{11}^{(d)} - V_{22}^{(d)})^2 + (V_{12}^{(d)})^2} \right]. \quad (10) $$
Note, that for vanishing coupling $V_{12}^{(d)}$ the diabatic and adiabatic functions are the same. There is always at least one coordinate $Q_i$ along which $V_{12}^{(d)}$ does not vanish. Distortion along this coordinate will lower the adiabatic energy and the theorem will be fulfilled. This coordinate is found by symmetry considerations, namely $\Gamma_{\phi_1^{(d)}} \times \Gamma_{\phi_2^{(d)}} \times \Gamma_{Q_i} \supset \Gamma_A$, where $\Gamma_A$ refers to the totally symmetric representation of the point group. The proof of the Jahn-Teller theorem was to show that such a $Q_i$ exists for any conceivable point group with degenerate $\Gamma_A$s.

Let us now follow a systematic approach by which such a diabatic potential matrix for a Jahn-Teller system can be developed. Here, the crude adiabatic approximation comes into play because we will assume that the wave functions maintain the symmetry properties they have at a reference geometry throughout the entire space.

The electronic wave function of an $E$ state consists of two linearly independent solutions, say $\phi_x$ and $\phi_y$, corresponding to the same eigenvalue. From basic linear algebra we know that any normalized linear combination of these two functions is again an eigenfunction with the same eigenvalue. The same is true for the coordinates, say $x$ and $y$. The two components $x$ and $y$ of the $e$ modes can be transformed into the complex plane by

$$Q_+ = x + iy$$
$$Q_- = x - iy.$$  \hspace{1cm} (11a)

Accordingly, a unitary transformation matrix

$$U^\dagger = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ 1 & -i \end{pmatrix}$$  \hspace{1cm} (12)

is defined and the two components of the degenerate state wave function are transformed by

$$U^\dagger \Psi_{\langle xy \rangle} = U^\dagger \left( \frac{\langle \Psi_x \rangle}{\langle \Psi_y \rangle} \right) = \frac{1}{\sqrt{2}} \left( \frac{\langle \Psi_x \rangle + i \langle \Psi_y \rangle}{\langle \Psi_x \rangle - i \langle \Psi_y \rangle} \right) = \left( \frac{\langle \Psi_+ \rangle}{\langle \Psi_- \rangle} \right) = \Psi_\pm.$$ \hspace{1cm} (13)

In the complex plane it is easy to see how a rotation operator $\hat{C}_n$ acts on $Q_\pm$ and $|\Psi_\pm\rangle$, respectively. Lets demonstrate this for the simplest case, a three-fold rotation axis and the corresponding operator $\hat{C}_3$:

$$\hat{C}_3 Q_+ = e^{+2\pi i/3} Q_+ \quad \text{and} \quad \hat{C}_3 Q_- = e^{-2\pi i/3} Q_-$$ \hspace{1cm} (14)

$$\hat{C}_3 \langle \Psi_+ \rangle = e^{+2\pi i/3} \langle \Psi_+ \rangle \quad \text{and} \quad \hat{C}_3 \langle \Psi_- \rangle = e^{-2\pi i/3} \langle \Psi_- \rangle$$ \hspace{1cm} (15a)

$$\hat{C}_3 |\Psi_+\rangle = e^{-2\pi i/3} |\Psi_+\rangle \quad \text{and} \quad \hat{C}_3 |\Psi_-\rangle = e^{+2\pi i/3} |\Psi_-\rangle.$$ \hspace{1cm} (15b)

In the next step, the coupling part of the electronic Hamiltonian $\hat{H}_{el}$ is expressed in the spectral representation in the eigenstates $\{|\Psi_+\rangle, |\Psi_-\rangle\}$ as

$$\hat{H}_{el} = \Psi_+^\dagger \hat{H} \Psi_+ = \sum_{i,j} |\Psi_i\rangle H_{ij} \langle \Psi_j | \quad (i, j = +, -)$$ \hspace{1cm} (16)
in which the matrix elements $H_{ij}$ correspond to $H_{ij} = \langle \Psi_i | \hat{H}_d | \Psi_j \rangle$ ($i, j = +, -$). These are the matrix elements which are now expanded as Taylor series in the nuclear coordinates according to

$$H_{ij} = \sum_{p+q=0}^{\infty} \frac{c_{p,q}^{(ij)}}{(p + q)!} Q_i^p Q_j^q \quad (i, j = +, -).$$

(17)

So far, no new insight is gained. However, we are now in the position to apply the $\hat{C}_3$ operator and enforce symmetry restrictions. The fundamental requirement is that $\hat{H}$ has to commute with all symmetry operators $\hat{S}$ of the respective point group and that the eigenvalues of $\hat{H}$ are invariant under the operations of $\hat{S}$. This is equivalent to the requirement that operation of any $\hat{S}$ on any term of expansion (16) must result in an eigenvalue of unity. This may be demonstrated on the Hamiltonian term corresponding to $H_{++}$:

$$\hat{C}_3 |\Psi_+\rangle Q_+^p Q_-^q \langle \Psi_+ | = e^{-2\pi i/3} e^{(p+q)2\pi i/3} e^{(-q)2\pi i/3} e^{2\pi i/3} |\Psi_+\rangle Q_+^p Q_-^q \langle \Psi_+ |.$$ 

(18)

Since $|\Psi_+\rangle Q_+^p Q_-^q \langle \Psi_+ |$ must be an eigenfunction of $\hat{C}_3$ with eigenvalue 1, one easily finds that in eq. (17) only expansion coefficients $c_{p,q}^{(++)}$ are non-vanishing, which fulfill the condition $(p - q) \mod 3 = 0$. Corresponding results are obtained for the other elements of the Hamiltonian and one ends up with a full electronic Hamiltonian that corresponds to the diabatic potential matrix in the complex coordinate representation. Of course, one has to check each term of the expansion not only for one but for all symmetry operators of the point group.

**Table 2: Non-vanishing terms of the Hamiltonian matrix in complex representation.**

<table>
<thead>
<tr>
<th>order</th>
<th>diagonal $H_{++} = H_{--}$</th>
<th>off-diagonal $H_{+-} = (H_{-+})^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$Q_+^0 Q_-^0$</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>–</td>
<td>$Q_+^0 Q_-^1$</td>
</tr>
<tr>
<td>2</td>
<td>$Q_+^1 Q_-^1$</td>
<td>$Q_+^2 Q_-^0$</td>
</tr>
<tr>
<td>3</td>
<td>$Q_+^3 Q_-^0$ and $Q_+^0 Q_-^3$</td>
<td>$Q_+^4 Q_-^2$ and $Q_+^2 Q_-^4$</td>
</tr>
<tr>
<td>4</td>
<td>$Q_+^2 Q_-^2$</td>
<td>$Q_+^4 Q_-^2$ and $Q_+^5 Q_-^0$</td>
</tr>
<tr>
<td>5</td>
<td>$Q_+^4 Q_-^1$ and $Q_+^1 Q_-^4$</td>
<td>$Q_+^2 Q_-^3$ and $Q_+^5 Q_-^3$</td>
</tr>
<tr>
<td>6</td>
<td>$Q_+^6 Q_-^0$ and $Q_+^3 Q_-^3$ and $Q_+^0 Q_-^6$</td>
<td>$Q_+^1 Q_-^5$ and $Q_+^4 Q_-^2$</td>
</tr>
<tr>
<td>:</td>
<td>:</td>
<td>:</td>
</tr>
</tbody>
</table>

In special cases the representation in complex coordinates may be convenient but often the real representation is favourable. In this case, the result is easily back-transformed by

$$\hat{H}_d = \Psi_+^\dagger U \hat{H} U \Psi_+ = \Psi_+^\dagger \hat{H} \Psi_+,$$

(19)
For the electronic Hamiltonian matrix, which in the end corresponds to the diabatic potential matrix, this leads to the factorized expression

\[ \mathcal{H} = U H \pm U^\dagger = \sum_{n=0}^{\infty} \frac{1}{n!} \left\{ \left( \begin{array}{cc} \mathcal{V}^{(n)} & 0 \\ 0 & \mathcal{V}^{(n)} \end{array} \right) + \left( \begin{array}{c} \mathcal{W}^{(n)} \\ \mathcal{Z}^{(n)} \end{array} \right) \right\}. \] (20)

All matrix elements \( \mathcal{V}^{(n)} \), \( \mathcal{W}^{(n)} \), and \( \mathcal{Z}^{(n)} \) are real functions of the real nuclear coordinates \( x \) and \( y \). The first few terms of these functions are given below. Note that the expansion coefficients \( \lambda_k^{(n)} \) must be the same for the \( \mathcal{W} \) and \( \mathcal{Z} \) functions which reflects the symmetry properties of the point group.

\[ \begin{align*}
\mathcal{V}^{(0)} &= a_1^{(0)} \\
\mathcal{V}^{(1)} &= 0 \\
\mathcal{V}^{(2)} &= a_1^{(2)} \left[ x^2 + y^2 \right] \\
\mathcal{V}^{(3)} &= a_1^{(3)} \left[ 2x^3 - 6xy^2 \right] \\
\mathcal{V}^{(4)} &= a_1^{(4)} \left[ x^4 + 2x^2y^2 + y^4 \right] \\
&\vdots
\end{align*} \] (21)

\[ \begin{align*}
\mathcal{W}^{(0)} &= 0 \\
\mathcal{W}^{(1)} &= \lambda_1^{(1)} x \\
\mathcal{W}^{(2)} &= \lambda_1^{(2)} \left[ x^2 - y^2 \right] \\
\mathcal{W}^{(3)} &= \lambda_1^{(3)} \left[ x^3 + xy^2 \right] \\
\mathcal{W}^{(4)} &= \lambda_1^{(4)} \left[ x^4 - 6x^2y^2 + y^4 \right] + \lambda_2^{(4)} \left[ x^4 - y^4 \right] \\
&\vdots
\end{align*} \] (22)

\[ \begin{align*}
\mathcal{Z}^{(0)} &= 0 \\
\mathcal{Z}^{(1)} &= \lambda_1^{(1)} y \\
\mathcal{Z}^{(2)} &= -2\lambda_1^{(2)} xy \\
\mathcal{Z}^{(3)} &= \lambda_1^{(3)} \left[ x^2y + y^3 \right] \\
\mathcal{Z}^{(4)} &= \lambda_1^{(4)} \left[ 4x^3y - 4xy^3 \right] + \lambda_2^{(4)} \left[ -2x^3y - 2xy^3 \right] \\
&\vdots
\end{align*} \] (23)
Besides Jahn-Teller there may also be pseudo-Jahn-Teller coupling active in a highly symmetric system. In its original sense, pseudo-Jahn-Teller coupling is the vibronic coupling between a degenerate and a nondegenerate state which is induced by a degenerate coordinate. The treatment of pseudo-Jahn-Teller coupling can follow a similar pattern to that of Jahn-Teller coupling. However, one has to keep in mind that now we have an inter-state rather than an intra-state coupling so that degeneracies between the nondegenerate and degenerate states would be by coincidence. Nevertheless, all the symmetry restrictions still apply.

Let us now derive the diabatic potential matrix for a prototypical \((A + E) \otimes e\) problem, again assuming a \(C_3\) rotational axis as main symmetry element. The two components \(x\) and \(y\) of the \(e\) mode are transformed into the complex plane according to eq. (11). The wave functions of the three state components, represented as vector \(\Psi_{(a12)}\), need also to be transformed into the complex plane similar to eq. (12). However, the transformation matrix now has to be a \(3 \times 3\) unitary matrix and the nondegenerate state remains real:

\[
U^\dagger \Psi_{(a12)} = \frac{1}{\sqrt{2}} \begin{pmatrix} \sqrt{2} & 0 & 0 \\ 0 & 1 & i \\ 0 & 1 & -i \end{pmatrix} \begin{pmatrix} \langle \Psi_a \rangle \\ \langle \Psi_1 \rangle \\ \langle \Psi_2 \rangle \end{pmatrix} = \begin{pmatrix} \langle \Psi_a \rangle \\ \langle \Psi_+ \rangle \\ \langle \Psi_- \rangle \end{pmatrix} = \Psi_{(a+-)}. \tag{24}
\]

In the next step, again the spectral representation of the electronic Hamiltonian

\[
\hat{H}_{el} = \Psi_{(a+-)}^\dagger \mathbf{H}_{(a+-)} \Psi_{(a+-)} = \sum_{i,j} |\Psi_i\rangle H_{ij} \langle \Psi_j| \quad (i, j = a, +, -) \tag{25}
\]
is used and the matrix elements $H_{ij} = \langle \Psi_i | \hat{H}_{el} | \Psi_j \rangle$ \((i, j = a, +, -)\) are expanded as Taylor series up to the required order in $Q_+$ and $Q_-$. For the $2 \times 2$ sub-block corresponding to the degenerate electronic state, of course exactly the same result is obtained as for the pure JT problem. The additional terms for the PJT coupling are analyzed in exactly the same way as for the JT case by applying the $\hat{C}_3$ operator on all terms of expansion eq. (25).

For example,

$$\hat{C}_3 |\Psi_a\rangle Q^p_+ Q^q_- \langle \Psi_+| = 1 \cdot e^{(p+q)2\pi i/3} \cdot e^{(q)p2\pi i/3} \cdot e^{-2\pi i/3} \cdot |\Psi_+\rangle Q^p_+ Q^q_- \langle \Psi_+|$$

(26)

can contribute only for $(p, q)$ combinations which fulfill the condition $(p-q-1) \mod 3 = 0$. It turns out that the nonvanishing $H_{a+}$ and $H_{a-}$ are of the same form as the $H_{+, -}$ and $H_{-, +}$ terms of the JT sub-block. Thus, after back-transformation by

$$\hat{H}_{el} = |\Psi_{(a+)}\rangle U^\dagger H_{(a+)} U |\Psi_{(a+)}\rangle = |\Psi_{(a12)}\rangle \mathcal{H} |\Psi_{(a12)}\rangle$$

(27)

one obtains exactly the same $\mathcal{V}^{(n)}_a$, $\mathcal{W}^{(n)}_a$, and $\mathcal{Z}^{(n)}_a$ functions in the real representation as were derived for the pure JT case. In the end, the full $3 \times 3$ diabatic potential matrix for the fully coupled JT and PJT problem is expressed by the factorized expansion

$$\mathcal{H} = U H U^\dagger = \sum_{n=0}^1 \frac{1}{n!} \left\{ \begin{array}{cc}
\mathcal{V}^{(n)}_A & 0 \\
0 & \mathcal{V}^{(n)}_E \\
0 & 0
\end{array} \right\} + \left\{ \begin{array}{ccc}
0 & 0 & 0 \\
0 & \mathcal{W}^{(n)}_{JT} & \mathcal{Z}^{(n)}_{JT} \\
0 & \mathcal{Z}^{(n)}_{JT} & -\mathcal{W}^{(n)}_{JT}
\end{array} \right\}$$

(28)

$$+ \sum_{n=0}^1 \frac{1}{n!} \left\{ \begin{array}{c}
\mathcal{V}^{(n)}_{PJT} \\
-\mathcal{Z}^{(n)}_{PJT} \\
\mathcal{Z}^{(n)}_{PJT}
\end{array} \right\}$$

(29)

What remains is to make sure that each term in eq. (28) also fulfills the invariance condition under all other symmetry operators $\hat{S}$ of the nuclear point group in question.

So far, we ignored the coordinates which do not couple the components of the degenerate states or the degenerate with nondegenerate states. All these coordinates will contribute to the representation of the diagonal potentials and can be added as functions $A^{(n)}$ with powers chosen appropriate to fulfill the symmetry requirements. Since $\hat{C}_n A^{(n)} = 1 \cdot A^{(n)}$ these terms can also be multiplied with the $\mathcal{V}$, $\mathcal{W}$, and $\mathcal{Z}$ terms. This can be utilized to improve the representation of the true potential energy surfaces by the Taylor expansions.

Going one step further, one can also treat inter-state couplings between two degenerate states, in which the $A$ functions become coupling functions. In this case the (symbolic)
coupling matrix reads

\[
\mathcal{H} = \sum_n \sum_m \frac{1}{n! m!} \begin{pmatrix}
\mathcal{V}_1^{(n)} + \mathcal{A}_1^{(m)} & 0 & 0 & 0 \\
0 & \mathcal{V}_1^{(n)} + \mathcal{A}_1^{(m)} & 0 & 0 \\
0 & 0 & \mathcal{V}_2^{(n)} + \mathcal{A}_2^{(m)} & 0 \\
0 & 0 & 0 & \mathcal{V}_2^{(n)} + \mathcal{A}_2^{(m)}
\end{pmatrix}
\]

[WE: multi-mode problems and mode-mode coupling ]

5 Some words on fitting Hamiltonian parameters

- Select model potential
  - Minimal models (e.g., linear vibronic coupling) and minimal fits for standard vibronic coupling spectra (large molecules, ultra-short dynamics)
  - Refined models for nonadiabatic dynamics studies (e.g., internal conversion): Higher-order, mode-mode couplings, PESs over extended regions.

- Choice of coordinates: Cartesian or curvilinear normal modes, symmetry coordinates, symmetrized Morse coordinates, etc.

- Accurate ab initio calculations of the PES along all required coordinates.

- Fit eigenvalues of diabatic matrix with respect to adiabatic ab initio energies. For matrices larger than $2 \times 2$ this requires a nonlinear optimization of the parameters in the potential matrix.

- Always fit $x$ and $y$ components simultaneously. Otherwise, the potential along the left out coordinate may be reproduced very badly (unless the applied model is nearly perfect).
Inter-state couplings (e. g. pseudo-Jahn-Teller) are obtained from the deviations of the true data points from the assumed diagonal potentials; intra-state couplings (e. g. Jahn-Teller) show up on the diagonal as well.

- Fitting strategy:
  - Build up the fit step by step.
  - Separate modes.
  - Start with low coupling orders.
  - Increase coupling orders.
  - Freeze parameters and fit mode-mode couplings or inter-state couplings (e. g. pseudo-Jahn-Teller).
  - Finally, unfreeze and get fully coupled results.

6 Applications and examples

The photoelectron spectrum of NH$_3$ shows two bands, one is well resolved, regular progression, the other is completely diffuse and congested. When ionizing to the second band, no fluorescence can be observed. Responsible for these findings is the presence of a $^2A_1$ and a $^2E$ state which are coupled by Jahn-Teller and pseudo-Jahn-Teller couplings. In fact, the ground state of NH$_3^+$ has a planar equilibrium geometry for which the states become $^2A_2^*$ and $^2E'$ among which no pseudo-Jahn-Teller coupling is possible. This system has been described by a diabatic potential matrix developed along the lines shown above.

The $3 \times 3$ diabatic potential energy matrix $V$ is expressed in symmetry-adapted coordinates $S$. $S_1$ refers to totally symmetric stretching, $S_2$ corresponds to the umbrella motion, $S_3, S_4$ are the components of the $e'$ stretching, and $S_5, S_6$ the components of the $e'$ bending mode. The potential matrix can be factorized into several contributions according to

$$V = V^{(S_1)} + V^{(S_2)} + V^{\text{diag}} + V^{JT} + V^{PJT}. \quad (31)$$

Besides the terms originating from JT and PJT coupling, we have contributions from pure potential functions along coordinates $S_1$ and $S_2$. The potentials along the totally symmetric $S_1$ coordinate are given by the diagonal matrix

$$V^{(S_1)} = \begin{pmatrix}
V_A^{(S_1)} & 0 & 0 \\
0 & V_E^{(S_1)} & 0 \\
0 & 0 & V_E^{(S_1)}
\end{pmatrix} \quad (32)$$
and the matrix elements correspond to modified Morse functions

\[ V_j^{(S_1)} = D_j^{(2)} \{ 1 - \exp \left[ -\alpha_j (r_j - S_1) \right] \}^2 + D_j^{(3)} \{ 1 - \exp \left[ -\alpha_j (r_j - S_1) \right] \}^3 - D_j^{(2)} \{ 1 - \exp [ -\alpha_j r_j] \}^2 - D_j^{(3)} \{ 1 - \exp [ -\alpha_j r_j] \}^3 \quad (j = A, E) \quad (33) \]

for the \(^2A''\) and \(^2E'\) states. The potentials along the umbrella coordinate \(S_2\) are approximated by the power series

\[ V^{(S_2)} = \sum_{n=1}^{\infty} \frac{1}{(2n)!} \begin{pmatrix} u_A^{(n)} & 0 & 0 \\ 0 & u_E^{(n)} & 0 \\ 0 & 0 & u_E^{(n)} \end{pmatrix} S_2^{2n} \quad (34) \]

in which the \(^2A''\) and \(^2E'\) states are represented by different sets of parameters, \(u_A\) and \(u_E\). The potential part corresponding to the \(e\) modes is split into three matrices which correspond to a diagonal part, the JT, and the PJT coupling. The diagonal contribution is expressed by the matrix

\[ V^{\text{diag}} = \begin{pmatrix} V_A^{\text{diag}} & 0 & 0 \\ 0 & V_E^{\text{diag}} & 0 \\ 0 & 0 & V_E^{\text{diag}} \end{pmatrix}, \quad (35) \]

with the diagonal elements expanded as

\[ V_j^{\text{diag}} = \sum_{n=0}^{\infty} \frac{1}{n!} V_j^{(n)} (S_3, S_4) + \sum_{n=0}^{\infty} \frac{1}{n!} V_j^{(n)} (S_5, S_6) \quad (j = A, E). \quad (36) \]

The contribution by JT coupling is given by

\[ V^{\text{JT}} = \sum_{j=3,5} \sum_{n=1}^{\infty} \frac{1}{n!} \begin{pmatrix} 0 & 0 & 0 \\ 0 & Z_j^{(n)} (S_j, S_{j+1}) & Z_j^{(n)} (S_j, S_{j+1}) \\ 0 & Z_j^{(n)} (S_j, S_{j+1}) & -Z_j^{(n)} (S_j, S_{j+1}) \end{pmatrix}, \quad (37) \]

and finally the coupling due to the PJT effect reads as

\[ V^{\text{PJT}} = S_2 \sum_{j=3,5} \sum_{n=1}^{\infty} \frac{1}{n!} \begin{pmatrix} 0 & W_j^{(n)} (S_j, S_{j+1}) & -Z_j^{(n)} (S_j, S_{j+1}) \\ W_j^{(n)} (S_j, S_{j+1}) & 0 & 0 \\ -Z_j^{(n)} (S_j, S_{j+1}) & 0 & 0 \end{pmatrix}. \quad (38) \]

It has to be noted that the entire latter matrix is multiplied by the umbrella coordinate \(S_2\) to account for the dependence of the PJT coupling on the umbrella angle, as discussed above. The definition of \(S_2\) is chosen such that \(S_2 = 0\) corresponds to the planar configuration. The evolution of the adiabatic ground state population after ionization to the excited state is presented in Figure 5 up to 100 fs.
Figure 2: Adiabatic (solid lines) and diabatic (dashed lines) energies (in eV) as a function of the $S_5$ coordinate (upper panel) and the combined $S_5, S_6$ ($S_6 = \frac{3}{5\sqrt{3}}S_5$) coordinates (lower panel, $S_5$ plotted) at pyramidal geometry are compared to \textit{ab initio} data (open circles).
Figure 3: First band of the photoelectron spectrum of NH₃: experimental spectrum (top panel) and present result (bottom panel).
Figure 4: Second band of the photoelectron spectrum of NH₃: experimental spectrum (top panel) and present result (bottom panel).

Figure 5: Adiabatic electronic population of the ground state of NH₃⁺ after excitation into one of the diabatic excited state, as a function of time in fs.
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