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

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(With special regards to Z. L.)

The Jahn-Teller effect came into life shortly after the Big Bang, together with the first polyatomic molecules. Unfortunately, there were no scientists around to witness this seminal event.

$$\text{No exact birth date} \Rightarrow \text{no birthday party} \tag{1}$$

It took > 13 billion years to discover this effect. The birth date of Edward Teller is known (Jan. 15, 1908 in Budapest), but he did not discover the effect 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.

He started immediately to work on this problem with his student Hermann Arthur Jahn (born May 31, 1907 in Colchester, Essex, died 1979 in Southampton). For all conceivable symmetries of molecules they found no exceptions from Landau's theorem. The siuation for linear molecules has been investigated before by R. Renner [*Z. Phys.* **92** (1934) 172].

Theorem: Jahn-Teller theorem

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

This was indeed the first treatment of conical intersections, published in 1937 [H. A. Jahn, E. Teller, *Proc. Royal Soc. London* **161** (1937) 220]. This intriguing subject has fascinated scientists ever since.

Other nice things we owe to Teller: 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 througout his life, later probably 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 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.* superfluidity). The same year, he was involved in a bad car accident from which he never recovered and died on April 1, 1968.

A set $\mathbb{G}$ with elements a, b is *closed* with respect to the operation $\circ$ if

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

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:

1. $a \circ (b \circ c) = (a \circ b) \circ c \qquad \forall \quad a, b, c \in \mathbb{G}$ (associative).

2. It exits a *neutral element* $e \in \mathbb{G}$ with $e \circ a = a \quad \forall \quad a \in \mathbb{G}$.

3. For each element $a \in \mathbb{G}$ there exists an inverse element $a^{-1} \in \mathbb{G}$ with $a \circ a^{-1} = a^{-1} \circ a = e$.

Definition:

A group is called Abelian if

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

i. e. if elements a, b commute with respect to $\circ$.

Corollar:

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

Theorem:

The representation of any point group, containing a rotational axis C_n with $n > 2$, contains at least one *degenerate* irreducible representation. Thus, such a point group is *non-Abelian*.

Corollar:

Action of any symmetry operator $\widehat{S}_k$ on the molecule belonging to point group $\mathbb{G}$ does not change the physics of the system.

$$\therefore \qquad [\widehat{H}, \widehat{S}_k] = 0, \qquad \forall \quad \widehat{S}_k \in \mathbb{G}.$$

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

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$\alpha_{xx} + \alpha_{yy},\ \alpha_{zz}$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	$(T_x,\ T_y)$	$(\alpha_{xx} - \alpha_{yy},\ \alpha_{xy})$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	T_z	
E''	2	-1	0	-2	1	0	$(R_x,\ R_y)$	$(\alpha_{xy},\ \alpha_{zx})$

Coupled Schrödinger equation in the adiabatic representation:

$$[\widehat{T}_n \mathbf{1} + \mathbf{V}(\mathbf{Q}) - E\mathbf{1}]\chi(\mathbf{Q}) = \mathbf{\Lambda}\chi(\mathbf{Q}). \tag{2}$$

$\widehat{T}_n$ is the nuclear kinetic operator, $\mathbf{V}(\mathbf{Q})$ the diagonal adiabatic PE matrix, $\chi(\mathbf{Q})$ the nuclear wave function vector, and $\mathbf{\Lambda}$ the nonadiabatic coupling matrix. The matrix elements λ_{ij} are expressed as

$$\Lambda_{ij} = -\langle\phi_i|\widehat{T}_n|\phi_j\rangle + \langle\phi_i|\nabla|\phi_j\rangle\nabla, \tag{3}$$

where ϕ are the adiabatic electronic wave functions which are eigenfunctions of the electronic Hamiltonian

$$\widehat{H}_e\phi_i(\mathbf{r}, \mathbf{Q}) = V_i(\mathbf{Q})\phi_i(\mathbf{r}, \mathbf{Q}) \tag{4}$$

The full adiabatic molecular wave function can be expanded as

$$\Psi(\mathbf{r}, \mathbf{Q}) = \sum_i \phi_i(\mathbf{r}, \mathbf{Q})\chi_i(\mathbf{Q}). \tag{5}$$

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The Λ_{ij} diverge at a conical intersection.

$\Rightarrow$ Change to diabatic representation:

$$\Psi(\mathbf{r}, \mathbf{Q}) = \phi^\dagger \mathbf{U}\mathbf{U}^\dagger \chi = (\mathbf{U}^\dagger \phi)^\dagger \, \mathbf{U}^\dagger \chi = \phi^{(d)\dagger} \chi^{(d)}. \qquad (6)$$

To simplify the coupled Schrödinger equation eq. (2) we chose $\nabla \mathbf{U} + \mathbf{F}\mathbf{U} = 0$ ($F_{ji} = \langle \phi_j | \nabla \phi_i \rangle$, $\{\phi_k\}$ is a complete basis) and we get after some math

$$\left[(\mathbf{V} - E\mathbf{1})\mathbf{U} - \frac{\hbar^2}{2m}\mathbf{U}\nabla^2 \right] \chi^{(d)} = 0. \qquad (7)$$

We can multiply with $\mathbf{U}^\dagger$ from the left and obtain the working equations in the diabatic basis

$$\left[\mathbf{V}^{(d)} - E\mathbf{1} - \frac{\hbar^2}{2m}\nabla^2 \right] \chi^{(d)} = 0. \qquad (8)$$

The diabatic potential matrix $\mathbf{V}^{(d)} = \mathbf{U}^{\dagger}\mathbf{V}\mathbf{U}$ is no longer diagonal. The main issue is to find the appropriate adiabatic-to-diabatic transformation $\mathbf{U}$.

We now introduce the **crude adiabatic approximation**

$$\Psi(\mathbf{r}, \mathbf{Q})^{crude} = \sum_i \phi_i^0(\mathbf{r}, \mathbf{Q_0})\chi_i^0(\mathbf{Q}). \tag{9}$$

The total wave function at any point $\mathbf{Q}$ is expressed using the electronic wave functions ϕ_i^0 at the reference point $\mathbf{Q}_0$. Jahn-Teller and *pseudo*-Jahn-Teller Hamiltonians can be derived using the symmetry of ϕ_i^0 at $\mathbf{Q}_0$.

H. C. Longuet-Higgins, *Adv. Spectrosc.*, **2** (1961) 429.

Theorem: Jahn and Teller, 1937

All non-linear nuclear configurations are . . . unstable for an orbitally degenerate electronic state.

Why is this the case? We know that in the adiabatic representation $\mathbf{V}(\mathbf{Q})$ is diagonal and therefore

$$\det \begin{pmatrix} V_{11}^{(d)} - V_1 & V_{12}^{(d)} \\ V_{12}^{(d)} & V_{22}^{(d)} - V_2 \end{pmatrix} \stackrel{!}{=} 0 \qquad (10)$$

The solution for the adiabatic potentials is

$$V_{1/2} = \frac{1}{2} \left[\left(V_{11}^{(d)} + V_{22}^{(d)} \right) \pm \sqrt{\left(V_{11}^{(d)} - V_{22}^{(d)} \right)^2 + \left(V_{12}^{(d)} \right)^2} \right]. \qquad (11)$$

Note, that for vanishing coupling $V_{12}^{(d)}$ the diabatic and adiabatic functions are the same.

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The coordinate along which $V_{12}^{(d)} \neq 0$ is found by symmetry considerations, namely

$$\Gamma_{\phi_1^{(d)}} \times \Gamma_{\phi_2^{(d)}} \times \Gamma_{Q_i} \supset \Gamma_A \qquad (\Gamma_A \equiv \text{totally symmetric}).$$

x and y shall transform like a degenerate irrep.

Transformation into the complex plane:

$$Q_+ = x + iy \qquad (12a)$$

$$Q_- = x - iy. \qquad (12b)$$

ϕ_x and ϕ_y are linearly independent electronic eigenfunctions with the same eigenvalue and $\Psi_x = \phi_x \chi_x$ etc. A unitary transformation matrix

$$\mathbf{U}^\dagger = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ 1 & -i \end{pmatrix} \tag{13}$$

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

$$\boldsymbol{U}^\dagger \boldsymbol{\Psi}_{(xy)} = \mathbf{U}^\dagger \begin{pmatrix} \langle\Psi_x| \\ \langle\Psi_y| \end{pmatrix} = \frac{1}{\sqrt{2}} \begin{pmatrix} \langle\Psi_x| + i\langle\Psi_y| \\ \langle\Psi_x| - i\langle\Psi_y| \end{pmatrix} = \begin{pmatrix} \langle\Psi_+| \\ \langle\Psi_-| \end{pmatrix} = \boldsymbol{\Psi}_{\pm}. \tag{14}$$

In the complex plane we can check the action of an arbitrary rotation operator $\widehat{C}_n$.

E. g. $\widehat{C}_3$:

$$\widehat{C}_3 Q_+ = e^{+2\pi i/3} Q_+ \quad \text{and} \quad \widehat{C}_3 Q_- = e^{-2\pi i/3} Q_- \tag{15}$$

$$\widehat{C}_3 \langle \Psi_+ | = e^{+2\pi i/3} \langle \Psi_+ | \quad \text{and} \quad \widehat{C}_3 \langle \Psi_- | = e^{-2\pi i/3} \langle \Psi_- | \tag{16a}$$

$$\widehat{C}_3 | \Psi_+ \rangle = e^{-2\pi i/3} | \Psi_+ \rangle \quad \text{and} \quad \widehat{C}_3 | \Psi_- \rangle = e^{+2\pi i/3} | \Psi_- \rangle. \tag{16b}$$

Now expand the electronic Hamiltonian $\widehat{H}_{el}$ in the spectral representation in the eigenstates $\{ |\Psi_+\rangle, |\Psi_-\rangle \}$ as

$$\widehat{H}_{el} = \mathbf{\Psi}_\pm^\dagger \mathbf{H}_\pm \mathbf{\Psi}_\pm = \sum_{i,j} |\Psi_i\rangle H_{ij} \langle \Psi_j| \qquad (i, j = +, -). \tag{17}$$

The matrix elements $H_{ij} = \langle \Psi_i | \widehat{H}_{el} | \Psi_j \rangle$ are expanded as Taylor series in the nuclear coordinates:

$$H_{ij} = \sum_{p+q=0} \frac{c_{p,q}^{(ij)}}{(p+q)!} \; Q_i^p Q_j^q \qquad (i,j = +,-). \qquad (18)$$

Since $[\widehat{H}, \widehat{S}_k] = 0$, operation of any $\hat{S}_k$ on any term of expansion (17) must result in an eigenvalue of unity.
For example H_{++}:

$$\hat{C}_3 | \Psi_+ \rangle Q_+^p Q_-^q \langle \Psi_+ | = e^{-2\pi i/3} e^{(+p)2\pi i/3} e^{(-q)2\pi i/3} e^{2\pi i/3} | \Psi_+ \rangle Q_+^p Q_-^q \langle \Psi_+ |. \qquad (19)$$

$$\Rightarrow \quad c_{p,q}^{(++)} \neq 0 \quad \forall \quad (p-q) \mod 3 = 0.$$

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

order	diagonal $H_{++} = H_{--}$	off-diagonal $H_{+-} = (H_{-+})^*$
0	$Q_+^0 Q_-^0$	—
1	—	$Q_+^0 Q_-^1$
2	$Q_+^1 Q_-^1$	$Q_+^2 Q_-^0$
3	$Q_+^3 Q_-^0$ and $Q_+^0 Q_-^3$	$Q_+^1 Q_-^2$
4	$Q_+^2 Q_-^2$	$Q_+^0 Q_-^4$ and $Q_+^3 Q_-^1$
5	$Q_+^4 Q_-^1$ and $Q_+^1 Q_-^4$	$Q_+^2 Q_-^3$ and $Q_+^5 Q_-^0$
6	$Q_+^6 Q_-^0$ and $Q_+^3 Q_-^3$ and $Q_+^0 Q_-^6$	$Q_+^1 Q_-^5$ and $Q_+^4 Q_-^2$
⋮	⋮	⋮

Usually the real representation is favourable, which is obtained by

$$\hat{H}_{el} = \mathbf{\Psi}_\pm^\dagger \boldsymbol{U}^\dagger \boldsymbol{U} H_\pm \boldsymbol{U}^\dagger \boldsymbol{U} \Psi_\pm = \mathbf{\Psi}_{(xy)}^\dagger \mathcal{H} \mathbf{\Psi}_{(xy)}. \tag{20}$$

This leads to the factorized expression

$$\mathcal{H} = \mathbf{U}\mathbf{H}_\pm\mathbf{U}^\dagger = \sum_{n=0} \frac{1}{n!} \left\{ \begin{pmatrix} \mathcal{V}^{(n)} & 0 \\ 0 & \mathcal{V}^{(n)} \end{pmatrix} + \begin{pmatrix} \mathcal{W}^{(n)} & \mathcal{Z}^{(n)} \\ \mathcal{Z}^{(n)} & -\mathcal{W}^{(n)} \end{pmatrix} \right\}. \tag{21}$$

All matrix elements $\mathcal{V}^{(n)}$, $\mathcal{W}^{(n)}$, and $\mathcal{Z}^{(n)}$ are real functions of the real nuclear coordinates x and y.

Lets have a look at the first few of these functions which
represent the uncoupled potentials:

$$\mathcal{V}^{(0)} = a_1^{(0)} \tag{22a}$$

$$\mathcal{V}^{(1)} = 0 \tag{22b}$$

$$\mathcal{V}^{(2)} = a_1^{(2)} \left[x^2 + y^2 \right] \tag{22c}$$

$$\mathcal{V}^{(3)} = a_1^{(3)} \left[2x^3 - 6\, xy^2 \right] \tag{22d}$$

$$\mathcal{V}^{(4)} = a_1^{(4)} \left[x^4 + 2x^2y^2 + y^4 \right] \tag{22e}$$

$$\vdots$$

Here are some coupling terms. Note that the expansion coefficients $\lambda_k^{(n)}$ must be the same for $\mathcal{W}$ and $\mathcal{Z}$.

$$
\begin{align}
\mathcal{W}^{(0)} &= 0 \tag{23a}\\
\mathcal{W}^{(1)} &= \lambda_1^{(1)} x \tag{23b}\\
\mathcal{W}^{(2)} &= \lambda_1^{(2)} \left[x^2 - y^2 \right] \tag{23c}\\
\mathcal{W}^{(3)} &= \lambda_1^{(3)} \left[x^3 + xy^2 \right] \tag{23d}\\
\mathcal{W}^{(4)} &= \lambda_1^{(4)} \left[x^4 - 6x^2 y^2 + y^4 \right] + \lambda_2^{(4)} \left[x^4 - y^4 \right] \tag{23e}
\end{align}
$$

$$\vdots$$

$$
\begin{align}
\mathcal{Z}^{(0)} &= 0 \tag{24a}\\
\mathcal{Z}^{(1)} &= \lambda_1^{(1)} y \tag{24b}\\
\mathcal{Z}^{(2)} &= -2\lambda_1^{(2)} xy \tag{24c}\\
\mathcal{Z}^{(3)} &= \lambda_1^{(3)} \left[x^2 y + y^3 \right] \tag{24d}\\
\mathcal{Z}^{(4)} &= \lambda_1^{(4)} \left[4x^3 y - 4xy^3 \right] + \lambda_2^{(4)} \left[-2x^3 y - 2xy^3 \right] \tag{24e}
\end{align}
$$

$$\vdots$$

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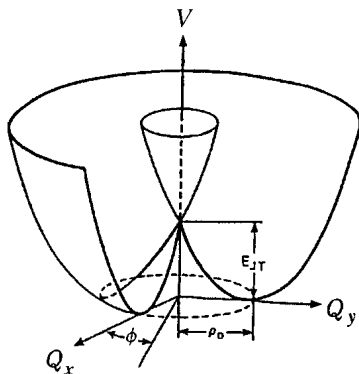
Figure: The well-known "Mexican hat" potential, arising from linear Jahn-Teller coupling. Note that this potential is cylindrically symmetric and lacks the n equivalent minima expected for systems with a C_n symmetry axis.

Definition:

pseudo-Jahn-Teller coupling is the vibronic coupling between a degenerate and a nondegenerate state which is induced by a degenerate mode. *pseudo*-Jahn-Teller is inter-state while Jahn-Teller is intra-state coupling.

Example: $(A + E) \otimes e$ *pseudo*-Jahn-Teller effect

Transform x and y into the complex plane according to eq. (12).

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

$$(25)$$

Use the spectral representation of the electronic Hamiltonian

$$\hat{H}_{el} = \boldsymbol{\Psi}^{\dagger}_{(a+-)}\boldsymbol{H}_{(a+-)}\boldsymbol{\Psi}_{(a+-)} = \sum_{i,j}|\Psi_i\rangle H_{ij}\langle\Psi_j| \qquad (i,j=a,+,-) \tag{26}$$

and expand the matrix elements $H_{ij} = \langle\Psi_i|\hat{H}_{el}|\Psi_j\rangle$
$(i,j=a,+,-)$ in Q_+ and Q_-.

$$\hat{C}_3|\Psi_a\rangle Q_+^p Q_-^q\langle\Psi_+| = 1\cdot e^{(+p)2\pi i/3}\cdot e^{(-q)2\pi i/3}\cdot e^{-2\pi i/3}\cdot |\Psi_a\rangle Q_+^p Q_-^q\langle\Psi_+| \tag{27}$$

$$\Rightarrow \quad c_{pq}^{(a+)} \neq 0 \qquad \forall \quad (p-q-1) \mod 3 = 0. \tag{28}$$

Back-transform by

$$\hat{H}_{el} = \boldsymbol{\Psi}^{\dagger}_{(a+-)}\boldsymbol{U}^{\dagger}\boldsymbol{U}H_{(a+-)}\boldsymbol{U}^{\dagger}\boldsymbol{U}\Psi_{(a+-)} = \boldsymbol{\Psi}^{\dagger}_{(a12)}\mathcal{H}\boldsymbol{\Psi}_{(a12)}. \tag{29}$$

We obtain exactly the same $\mathcal{V}^{(n)}$, $\mathcal{W}^{(n)}$, and $\mathcal{Z}^{(n)}$ functions as for JT. The fully coupled JT and PJT problem is expressed by the factorized expansion

$$
\begin{aligned}
\mathcal{H} &= \mathbf{U}\mathbf{H}\mathbf{U}^\dagger \\
&= \sum_{n=0} \frac{1}{n!} \left\{ \begin{pmatrix} \mathcal{V}_A^{(n)} & 0 & 0 \\ 0 & \mathcal{V}_E^{(n)} & 0 \\ 0 & 0 & \mathcal{V}_E^{(n)} \end{pmatrix} + \begin{pmatrix} 0 & 0 & 0 \\ 0 & \mathcal{W}_{JT}^{(n)} & \mathcal{Z}_{JT}^{(n)} \\ 0 & \mathcal{Z}_{JT}^{(n)} & -\mathcal{W}_{JT}^{(n)} \end{pmatrix} \right. \\
&\quad + \left. \begin{pmatrix} 0 & \mathcal{W}_{PJT}^{(n)} & -\mathcal{Z}_{PJT}^{(n)} \\ \mathcal{W}_{PJT}^{(n)} & 0 & 0 \\ -\mathcal{Z}_{PJT}^{(n)} & 0 & 0 \end{pmatrix} \right\} \qquad (30) \\
&= \sum_{n=0} \frac{1}{n!} \left\{ \mathbf{V}_{diag}^{(n)} + \mathbf{V}_{JT}^{(n)} + \mathbf{V}_{PJT}^{(n)} \right\}. \qquad (31)
\end{aligned}
$$

Non-degenerate coordinates can be added as functions $\mathcal{A}^{(n)}$ with

$$\widehat{C}_m \mathcal{A}^{(n)} = 1 \cdot \mathcal{A}^{(n)} \qquad (m > 2). \tag{32}$$

These terms can be multiplied with the $\mathcal{V}$, $\mathcal{W}$, and $\mathcal{Z}$ terms and added to the diagonal.

For inter-state couplings between two degenerate states, the $\mathcal{A}$ terms become coupling functions.

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

$$+ \begin{pmatrix} \mathcal{W}_1^{(n)} & \mathcal{Z}_1^{(n)} & 0 & 0 \\ \mathcal{Z}_1^{(n)} & -\mathcal{W}_1^{(n)} & 0 & 0 \\ 0 & 0 & \mathcal{W}_2^{(n)} & \mathcal{Z}_2^{(n)} \\ 0 & 0 & \mathcal{Z}_2^{(n)} & -\mathcal{W}_2^{(n)} \end{pmatrix}$$

$$+ \begin{pmatrix} 0 & 0 & \mathcal{W}_{12}^{(n)} & \mathcal{Z}_{12}^{(n)} \\ 0 & 0 & \mathcal{Z}_{12}^{(n)} & -\mathcal{W}_{12}^{(n)} \\ \mathcal{W}_{12}^{(n)} & \mathcal{Z}_{12}^{(n)} & 0 & 0 \\ \mathcal{Z}_{12}^{(n)} & -\mathcal{W}_{12}^{(n)} & 0 & 0 \end{pmatrix}$$

$$+ \begin{pmatrix} 0 & 0 & \mathcal{A}_{12}^{(m)} + \mathcal{V}_{12}^{(n)} & 0 \\ 0 & 0 & 0 & \mathcal{A}_{12}^{(m)} + \mathcal{V}_{12}^{(n)} \\ \mathcal{A}_{12}^{(m)} + \mathcal{V}_{12}^{(n)} & 0 & 0 & 0 \\ 0 & \mathcal{A}_{12}^{(m)} + \mathcal{V}_{12}^{(n)} & 0 & 0 \end{pmatrix} \quad (33)$$

The black magic of 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 2×2 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.

Application to photoionization dynamics of NH_3

- photoelectron spectrum of NH_3 shows two bands
- ground state band shows a well resolved, regular progression
- exited state band is completely diffuse and congested
- no fluorescence from upper state
- ionic ground state has planar equilibrium geometry
- state symmetries are $^2A_2''$ and $^2E'$ in D_{3h} and $^2A_1$ and ^2E in C_{3v}
- $\Rightarrow$ *pseudo*-Jahn-Teller coupling only possible for pyramidal geometries!

Coordinates:

$$S_1 = 3^{-1/2}(\Delta R_1 + \Delta R_2 + \Delta R_3) \qquad \text{sym. stretching} \qquad (34)$$

$$S_2 = \Delta\beta \qquad\qquad\qquad\qquad \text{umbrella} \qquad (35)$$

$$S_3 = 6^{-1/2}(2\Delta R_1 - \Delta R_2 - \Delta R_3) \qquad e'_x \text{ stretching} \qquad (36)$$

$$S_4 = 2^{-1/2}(\Delta R_2 - \Delta R_3) \qquad e'_y \text{ stretching} \qquad (37)$$

$$S_5 = 6^{-1/2}(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3) \qquad e'_x \text{ bending} \qquad (38)$$

$$S_6 = 2^{-1/2}(\Delta\alpha_2 - \Delta\alpha_3 \qquad\qquad e' \text{ bending} \qquad (39)$$

The potential matrix can be factorized into several contributions according to

$$\mathbf{V} = \mathbf{V}^{(S_1)} + \mathbf{V}^{(S_2)} + \mathbf{V}^{diag} + \mathbf{V}^{JT} + \mathbf{V}^{PJT}. \qquad (40)$$

The potentials along S_1 are given by the diagonal matrix $\mathbf{V}^{(S_1)}$ with elements $\mathbf{V}^{(S_1)}$ $(j = A, E)$

$$
\begin{aligned}
V_j^{(S_1)} &= D_j^{(2)}\{1 - \exp\left[-\alpha_j(r_j - S_1)\right]\}^2 \\
&+ D_j^{(3)}\{1 - \exp\left[-\alpha_j(r_j - S_1)\right]\}^3 \\
&- D_j^{(2)}\{1 - \exp\left[-\alpha_j r_j\right]\}^2 - D_j^{(3)}\{1 - \exp\left[-\alpha_j r_j\right]\}^3 \quad (41)
\end{aligned}
$$

The potentials along the umbrella coordinate S_2 are approximated by the power series

$$
\mathbf{V}^{(S_2)} = \sum_{n=1} \frac{1}{(2n)!}
\begin{pmatrix}
u_A^{(n)} & 0 & 0 \\
0 & u_E^{(n)} & 0 \\
0 & 0 & u_E^{(n)}
\end{pmatrix}
S_2^{2n}. \quad (42)
$$

The uncoupled diagonal contribution of the *e* modes is expressed by the matrix

$$\mathbf{V}^{diag} = \begin{pmatrix} V_A^{diag} & 0 & 0 \\ 0 & V_E^{diag} & 0 \\ 0 & 0 & V_E^{diag} \end{pmatrix}, \tag{43}$$

with the diagonal elements expanded as

$$V_j^{diag} = \sum_{n=0} \frac{1}{n!} \mathcal{V}_j^{(n)}(S_3, S_4) + \sum_{n=0} \frac{1}{n!} \mathcal{V}_j^{(n)}(S_5, S_6) \qquad (j = A, E). \tag{44}$$

The contribution by JT coupling is given by

$$\mathbf{V}^{JT} = \sum_{j=3,5} \sum_{n=1} \frac{1}{n!} \begin{pmatrix} 0 & 0 & 0 \\ 0 & \mathcal{W}_{JT}^{(n)}(S_j, S_{j+1}) & \mathcal{Z}_{JT}^{(n)}(S_j, S_{j+1}) \\ 0 & \mathcal{Z}_{JT}^{(n)}(S_j, S_{j+1}) & -\mathcal{W}_{JT}^{(n)}(S_j, S_{j+1}) \end{pmatrix},$$

$$(45)$$

and the coupling due to the PJT effect reads as

$$\mathbf{V}^{PJT} = S_2 \sum_{j=3,5} \sum_{n=1} \frac{1}{n!} \tag{46}$$

$$\begin{pmatrix} 0 & \mathcal{W}_{PJT}^{(n)}(S_j, S_{j+1}) & -\mathcal{Z}_{PJT}^{(n)}(S_j, S_{j+1}) \\ \mathcal{W}_{PJT}^{(n)}(S_j, S_{j+1}) & 0 & 0 \\ -\mathcal{Z}_{PJT}^{(n)}(S_j, S_{j+1}) & 0 & 0 \end{pmatrix}.$$

The PJT matrix is multiplied by S_2 ($S_2 = 0$: planar config.).

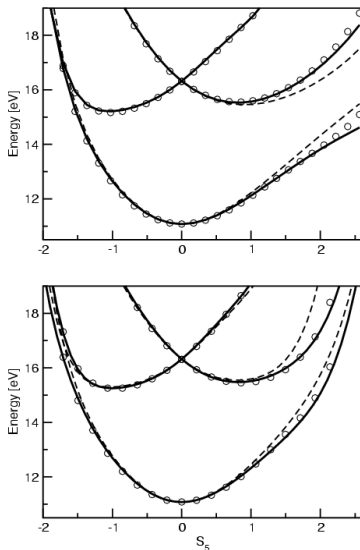Wolfgang Eisfeld   Treatment of Jahn-Teller and *pseudo*-Jahn-Teller effects

Figure: Adiabatic (solid) and diabatic energies along S_5 (a) and combined S_5, S_6 (b) at pyramidal geometry.
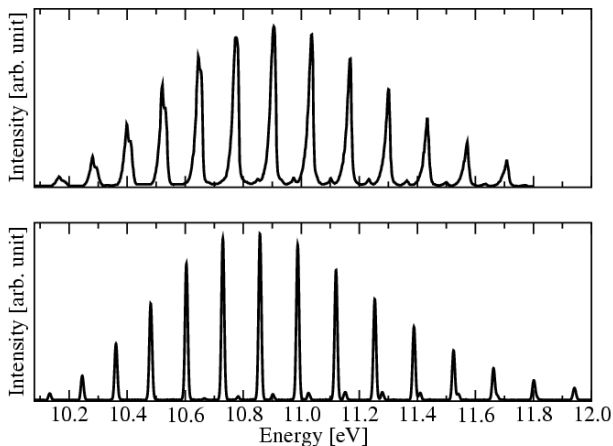
Figure: First band of the photoelectron spectrum of NH_3: experimental spectrum (top panel) and present result (bottom panel).
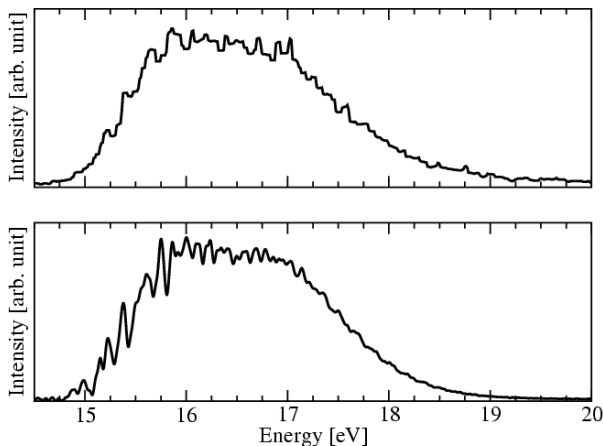
Figure: Second band of the photoelectron spectrum of NH_3:
experimental spectrum (top panel) and present result (bottom panel).

The evolution of the adiabatic ground state population after ionization to the excited state presented up to 100 fs.
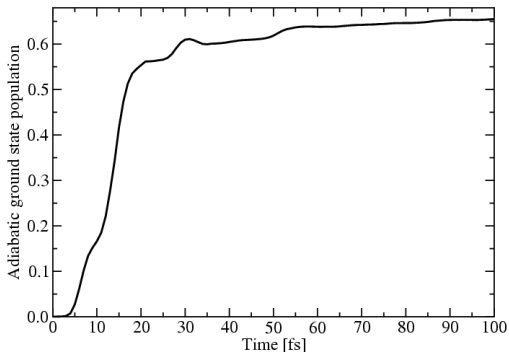

Figure: Adiabatic electronic population of the ground state of NH_3^+ after excitation into one of the diabatic excited state, as a function of time in fs.

Acknowledgments

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