

# Definitions of non adiabatic PES

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# Introduction

- Molecular system = Nuclei ( $\vec{R}$ , M) + Electrons ( $\vec{r}$ , m)
- PES = Potential energy function for nuclei created by the electrons
- “adiabatic” = depending upon a single electronic, quantum, pure state.
- “non-adiabatic” = depending upon more than one electronic state.

## Questions:

- Can a (single) PES be defined for a non-adiabatic/exact wave function, or, is the PES concept subordinated to a Born-Oppenheimer/Adiabatic approximation?
- What is the quantum/epistemological status of PES?

# Effective Non-Adiabatic Hamiltonian with single PES

- non-adiabatic PES dressed by excited electronic states

$$\lambda = \frac{m}{M}, \quad H = H_0 + \lambda H', \quad H \rightsquigarrow \exp(-i\lambda S) H \exp(i\lambda S),$$

$$H_{BM} = H_{BO} + \lambda \langle 0 | H' | 0 \rangle + \frac{i}{2} \lambda^2 \sum_{n \neq 0} (\langle 0 | H' | n \rangle \langle n | S | 0 \rangle - \langle 0 | S | n \rangle \langle n | H' | 0 \rangle)$$

Bunker and Moss, Mol. Phys. 33, p.417, (1977)

- geometry-dependent reduced vibrational and rotational masses

$$T_{\vec{R}} = T_{vib} + T_{rot}, \quad H_2^+, H_2 :$$

$$M_{red} = \frac{M_H}{2} \rightsquigarrow M_{vib} = M_{red} \left( 1 + \frac{A(\vec{R})}{M_H} \right)^{-1}, \quad M_{rot} = M_{red} \left( 1 + \frac{B(\vec{R})}{M_H} \right)^{-1}$$

Kutzelnigg, Mol. Phys. 105, p.2627, (2007)

# Density of probability for nuclei configurations in an isolated molecule

- for totally symmetrical rotational states

$$P(\vec{R}) := \int d\vec{r} \Psi^*(\vec{r}, \vec{R}) \Psi(\vec{r}, \vec{R})$$

$\vec{R}$  : translation-free nuclear variables,  $\vec{r}$  : electronic variables

- for non totally symmetrical rotational states

$$P(\vec{R}) := \int d\vec{r} \sum_{k=-J}^{+J} \Psi_k^*(\vec{r}, \vec{R}) \Psi_k(\vec{r}, \vec{R})$$

Hirschfelder and Wigner Proc. N. A. S. **21**, 113 (1935).

P. Cassam-Chenaï, J. Math. Chem. **23**, 61 (1998).

# Quotienting by the action of a symmetry group

- Ex.: rotations

$$\forall \mathcal{R} \in SO_3 \quad P\left(\mathcal{R}\left(\vec{R}\right)\right) = P\left(\vec{R}\right)$$

therefore the probability density,  $P$ , is a well-defined function,  $P\left(\widehat{R}\right)$ , of the sets of nuclear configurations equivalent modulo a rotation,  $\widehat{R} = \left\{\mathcal{R}\left(\vec{R}\right)\right\}_{\mathcal{R} \in SO_3}$ .

- The same reduction method applies to the group of permutations of identical nuclei

One obtains a partition of the nuclear configuration space into an infinite number of sets, each set corresponding to a distinct relative arrangement of the nuclei  $\left\{\widehat{R}\right\}$

# Hunter Generalised PES

- For  $J = 0$  in the Born-Oppenheimer approximation the wave function has the form,

$$\Psi(\vec{r}, \vec{R}) = \Psi_e(\vec{r}, \vec{R})\Psi_n(\vec{R})$$

and

$$P(\vec{R}) = \Psi_n^*(\vec{R})\Psi_n(\vec{R})$$

- For an arbitrary molecular wave function  $\Psi(\vec{r}, \vec{R})$  Hunter defines an “electronic” wave function by,

$$\Psi_e^{Hunter}(\vec{r}, \vec{R}) = \frac{\Psi(\vec{r}, \vec{R})}{\sqrt{P(\vec{R})}}$$

and

$$PES_{Hunter}(\vec{R}) := \int d\vec{r} \Psi_e^{Hunter*}(\vec{r}, \vec{R}) H^{mol}(\vec{r}, \vec{R}) \Psi_e^{Hunter}(\vec{r}, \vec{R})$$

# Wilson Generalised PES

- $$PES(\vec{R}) := \frac{\int d\vec{r} \sum_{k=-J}^{+J} \Psi_k^*(\vec{r}, \vec{R}) (T_e + V) \Psi_k(\vec{r}, \vec{R})}{P(\vec{R})}$$

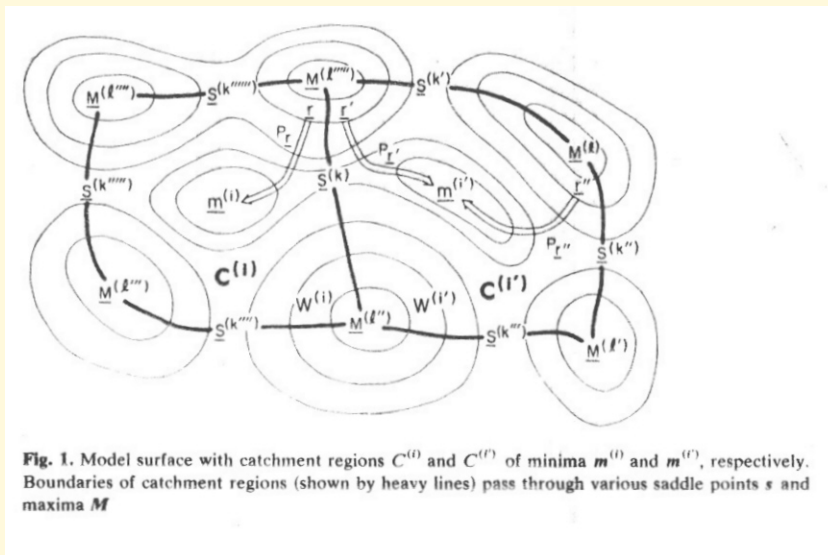
$$\forall \mathcal{R} \in SO_3 \quad PES(\mathcal{R}(\vec{R})) = PES(\vec{R}) =: PES(\widehat{R})$$

E. B. Wilson, Int. J. Quant. Chem. Symp. 13, p.5, (1979).

- Ex.: BO  $\Psi(\vec{r}, \vec{R}) = \Psi_n(\vec{R}) \Psi_e(\vec{r}, \vec{R})$   
with  $\forall \vec{R} \int d\vec{r} \Psi_e^*(\vec{r}, \vec{R}) \Psi_e(\vec{r}, \vec{R}) = 1$

$$PES(\vec{R}) = \int d\vec{r} \Psi_e^*(\vec{r}, \vec{R}) (T_e + V) \Psi_e(\vec{r}, \vec{R})$$

# Isomers and their structure



P.G. Mezey, *Theor. Chim. Acta.* **58**, 309 (1981).

- Isomer := attractor basin of  $PES(\hat{R})$
- Molecular structure of an isomer := nuclear arrangement at the minimum of the attractor basin



# Difficulty: excited vibrational states

- Ex.: non-adiabatic wave function for  $H_2$

$$\psi(\vec{\mathbf{r}}, R) = \phi_0(\vec{\mathbf{r}}, R)\chi_0(R) + \phi_1(\vec{\mathbf{r}}, R)\chi_1(R) ,$$

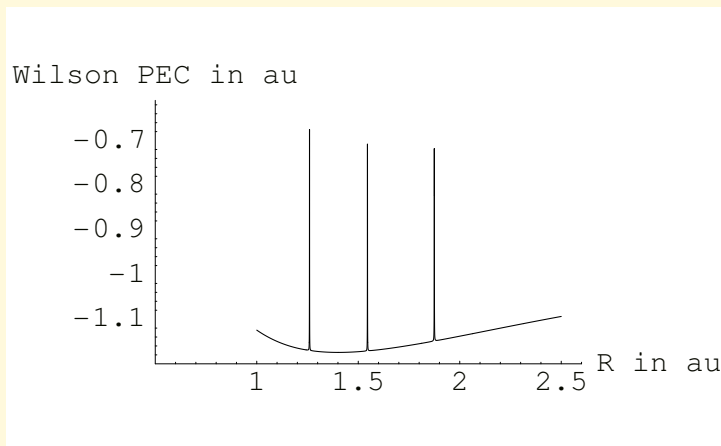
where  $\phi_0(\vec{\mathbf{r}}, R), \phi_1(\vec{\mathbf{r}}, R)$  are the solutions of the clamped nuclei Hamiltonians  $\hat{H}^{elec}(R)$  representing the  $X^1\Sigma_g^+$  and  $E, F^1\Sigma_g^+$  states respectively.

- Setting  $F_i(R) = R\chi_i(R)$ ,  $i \in \{0, 1\}$ , and  $\hat{H}' = \hat{H}^{mol} - \hat{H}^{elec}$ , the stationary Schrödinger equation gives the following set of coupled, eigenvalue equations,

$$\begin{aligned} \left[ -\frac{1}{m} \frac{d^2}{dR^2} + \hat{H}_{00}^{elec}(R) + \hat{H}'_{00}(R) - E \right] F_0(R) &= - \left[ \hat{H}'_{01}(R) - B(R) \frac{d}{dR} \right] F_1(R) \\ \left[ -\frac{1}{m} \frac{d^2}{dR^2} + \hat{H}_{11}^{elec}(R) + \hat{H}'_{11}(R) - E \right] F_1(R) &= - \left[ \hat{H}'_{10}(R) + B(R) \frac{d}{dR} \right] F_0(R) \end{aligned}$$

where  $B(R) := \frac{2}{m} \int \phi_0(\vec{\mathbf{r}}, R) \frac{d\phi_1(\vec{\mathbf{r}}, R)}{dR} d\vec{\mathbf{r}}$

- Solution for the  $\nu = 3$  vibrational state of the  $X^1\Sigma_g^+$  electronic state



P. Cassam-Chenai, Chem. Phys. Lett. **420**, 354-357 (2006).

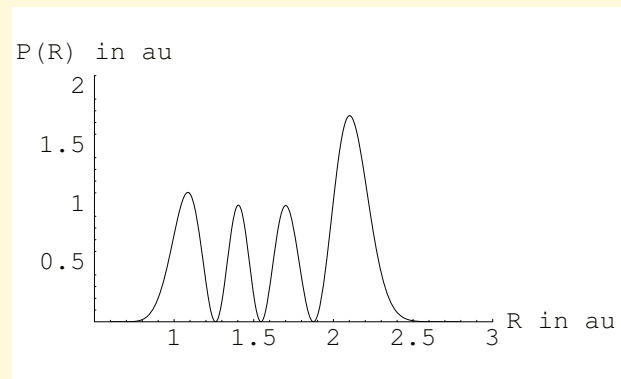
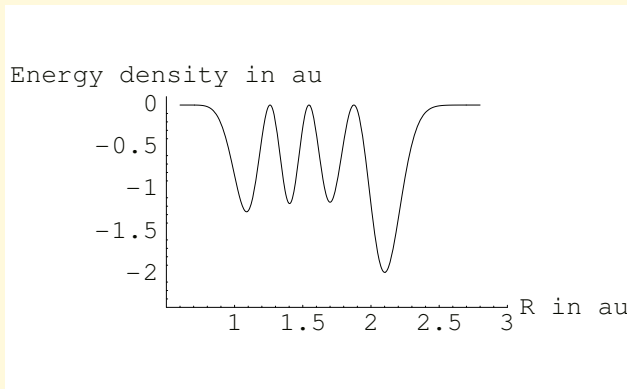
( For Hunter PES: J. Czub and L. Wolniewicz, Mol. Phys. **36**, 1301 (1978).)

- $$PES_{Wilson}(R) = \frac{F_0^2(R)\hat{H}_{00}^{elec}(R)+F_1^2(R)\hat{H}_{11}^{elec}(R)}{F_0^2(R)+F_1^2(R)}.$$

- Explanation:  $PES_{Wilson}(\vec{\mathbf{R}})$  should not be seen as the expectation value of an observable but as the ratio of the expectation values of two commuting observables

$$\hat{P}(\vec{\mathbf{R}}) := \int |\vec{\mathbf{r}}, \vec{\mathbf{R}}\rangle \langle \vec{\mathbf{r}}, \vec{\mathbf{R}}| d\vec{\mathbf{r}} \quad \mapsto \quad P(\vec{\mathbf{R}}) = \int \langle \psi | \vec{\mathbf{r}}, \vec{\mathbf{R}}\rangle \langle \vec{\mathbf{r}}, \vec{\mathbf{R}} | \psi \rangle d\vec{\mathbf{r}}$$

$$\hat{H}^{elec}(\vec{\mathbf{R}}) := \int \hat{H}^{elec}(\vec{\mathbf{r}}, \vec{\mathbf{R}}) |\vec{\mathbf{r}}, \vec{\mathbf{R}}\rangle \langle \vec{\mathbf{r}}, \vec{\mathbf{R}}| d\vec{\mathbf{r}} \quad \mapsto \quad E^{elec}(\vec{\mathbf{R}}) := \langle \psi | \hat{H}^{elec}(\vec{\mathbf{R}}) | \psi \rangle$$



# Conclusion

- The PES concept is not subordinated to a Born-Oppenheimer/Adiabatic approximation in Bunker and Moss or Kutzelnigg approaches but it is still an approximate concept valid only for low  $\frac{m}{M}$ .
- PES can be defined for a non-adiabatic/exact wave function in Hunter or Wilson approaches, but they are not quantum observables.

Questions are a burden to others, Answers a prison for oneself: