Thermodynamic properties of Nonadiabatic systems

Neil Raymond

Supervisors: Pierre-Nicholas Roy, Marcel Nooijen

Overview

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- Quantum Thermodynamics
  - Current Methods

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  - Define nonadiabatic

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- Theoretical Developments
  - Path Integral formulation

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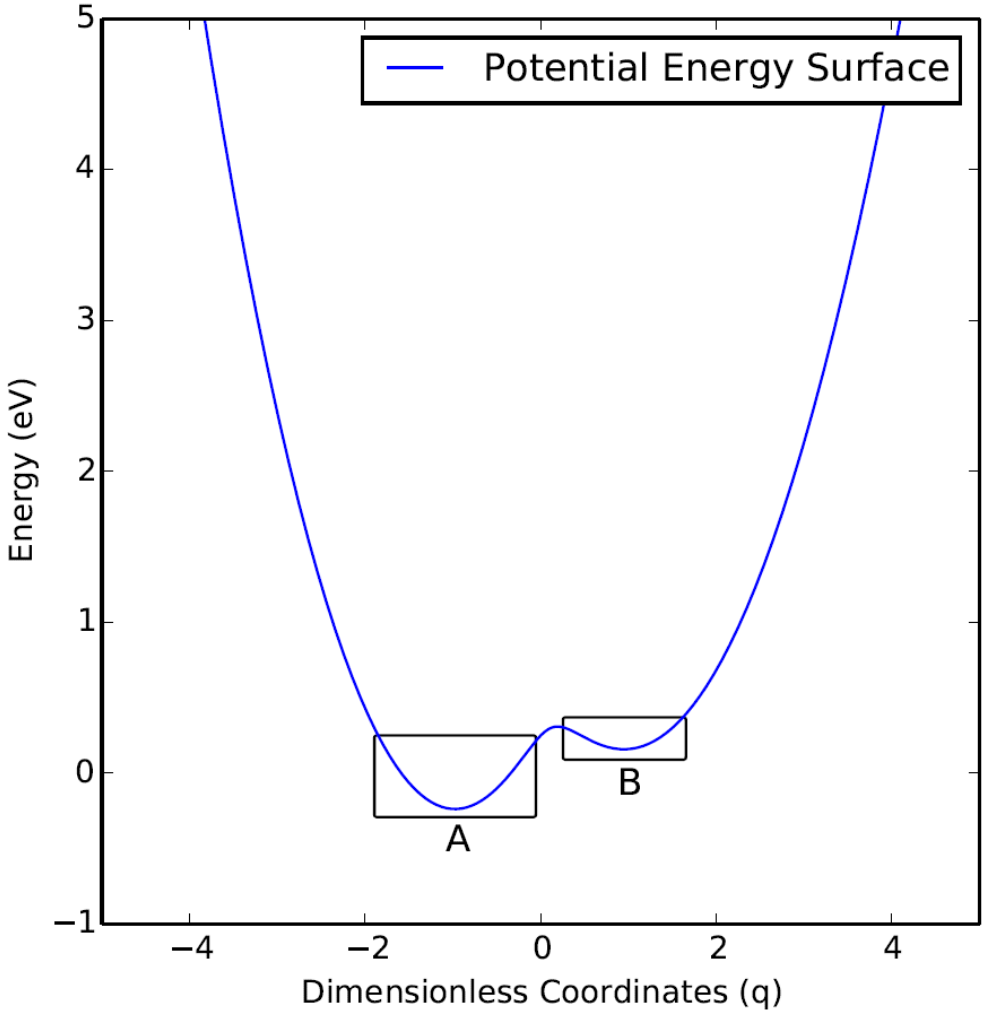
- Current Progress

Thermodynamics

- Gibbs energy $G \equiv A + k_B T$
  - measures the maximum or reversible work that may be performed by a thermodynamic system at a constant temperature and pressure



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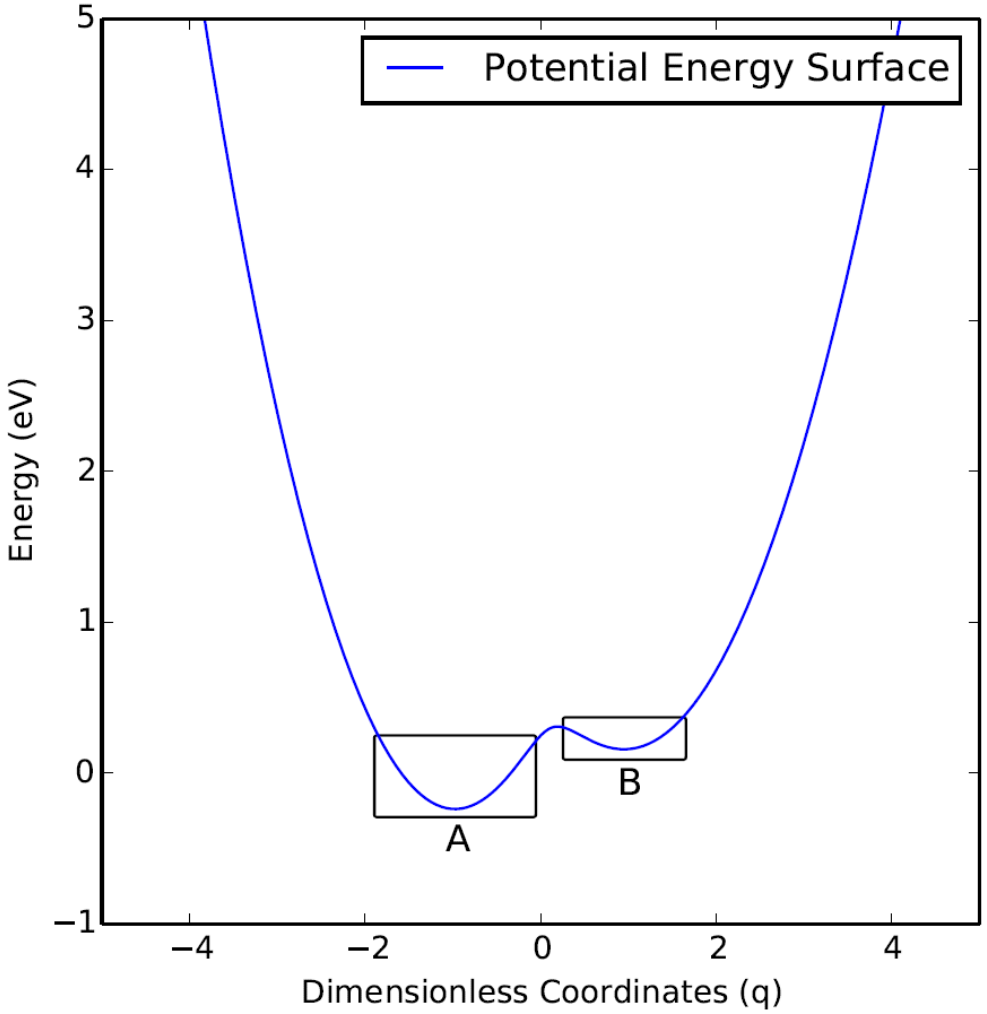

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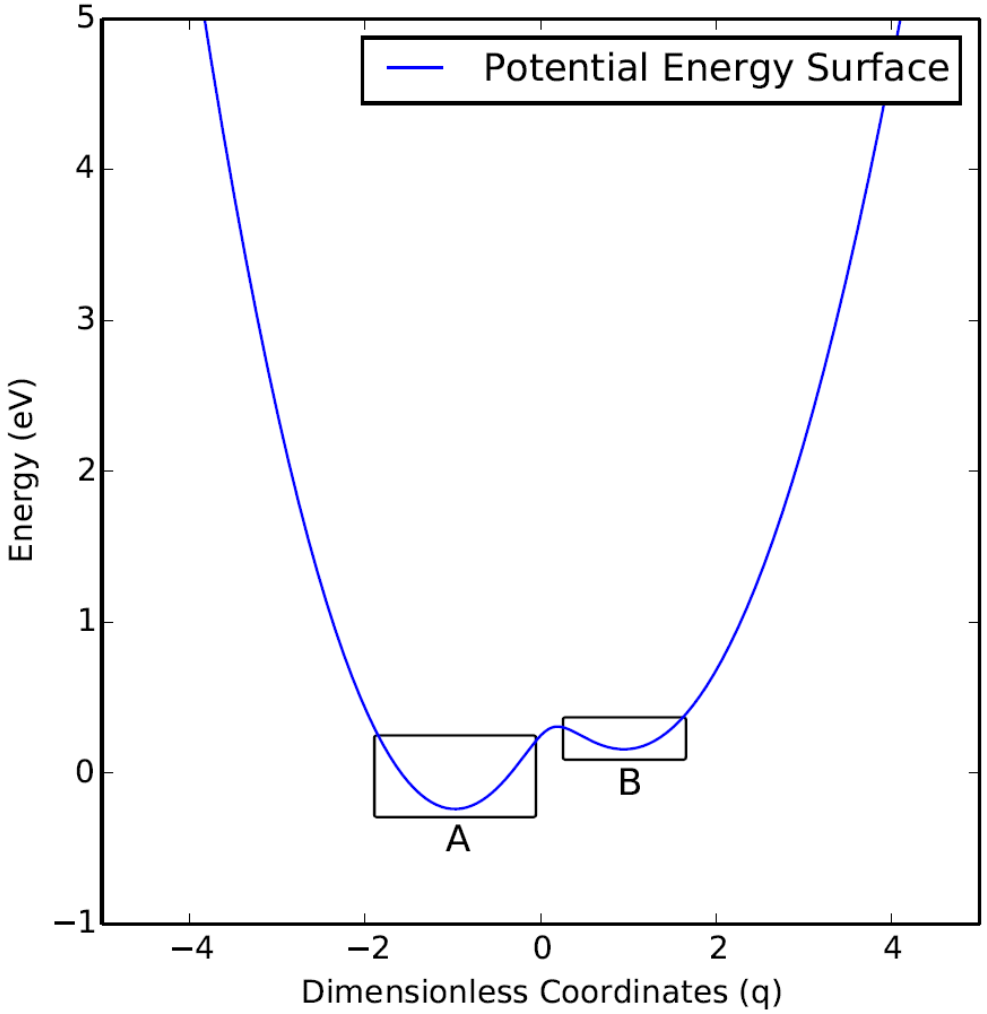
- Molecular-scale systems $RT = k_B T \times N_A$



Quantum Thermodynamics

Partition function: $Z = \sum_s e^{-\beta E_s}$

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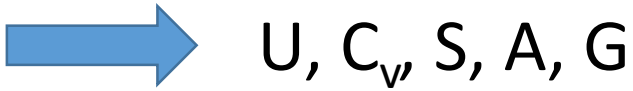
Thermodynamic properties expressed in terms of Z

$A = -k_B T \ln(Z)$	$C_v = \frac{1}{k_B T^2}\left(\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left[\frac{-1}{Z}\frac{\partial Z}{\partial \beta}\right]^2\right)$
$S = \frac{\partial}{\partial T}\left(k_B T \ln(Z)\right)$	$U = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial \ln(Z)}{\partial \beta}$

Electronic Structure Calculation



Exact solutions are hard to obtain

Electronic Structure Calculation

Z ⟹ U, C_v, S, A, G

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$$Z = Z_t \times Z_R \times Z_N \times Z_v \times Z_e$$

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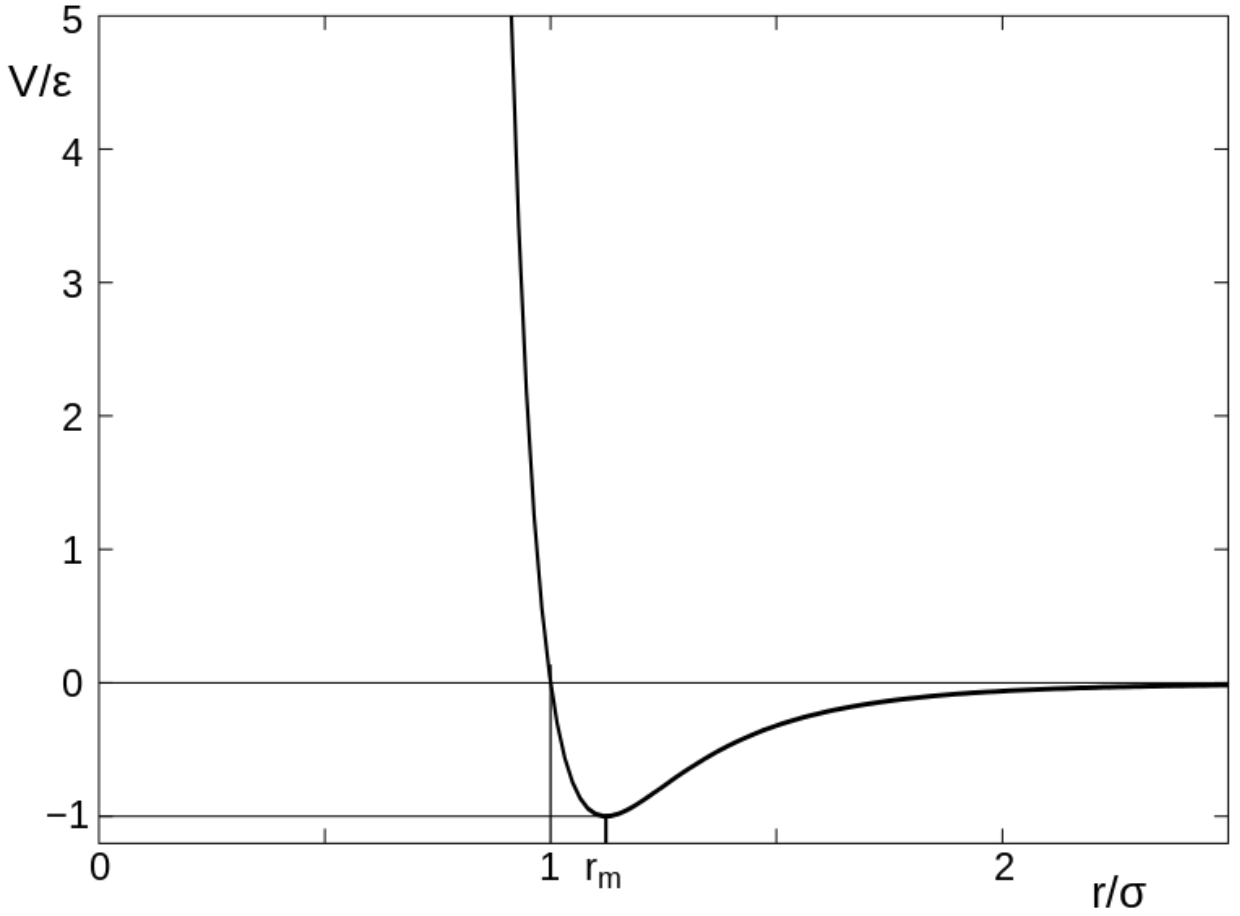

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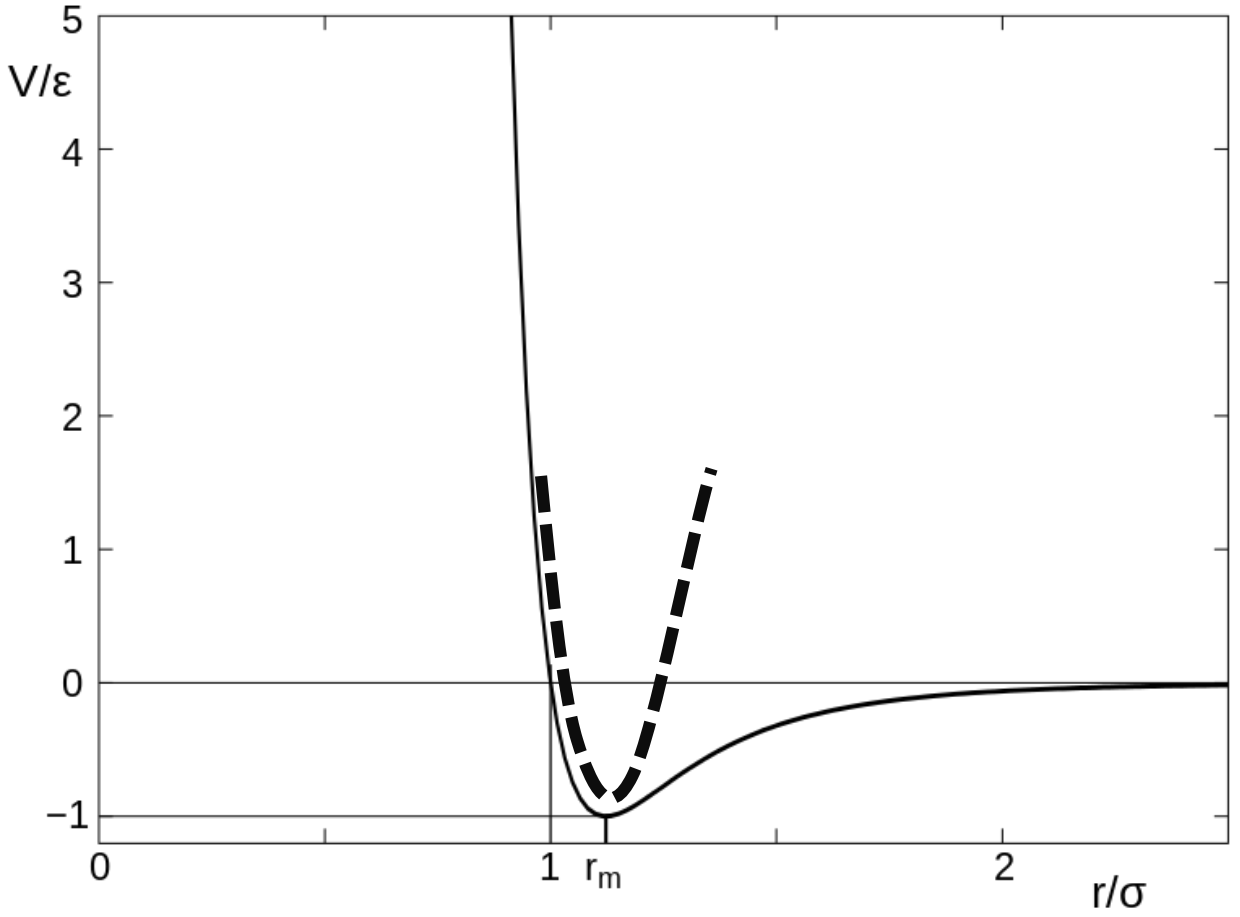

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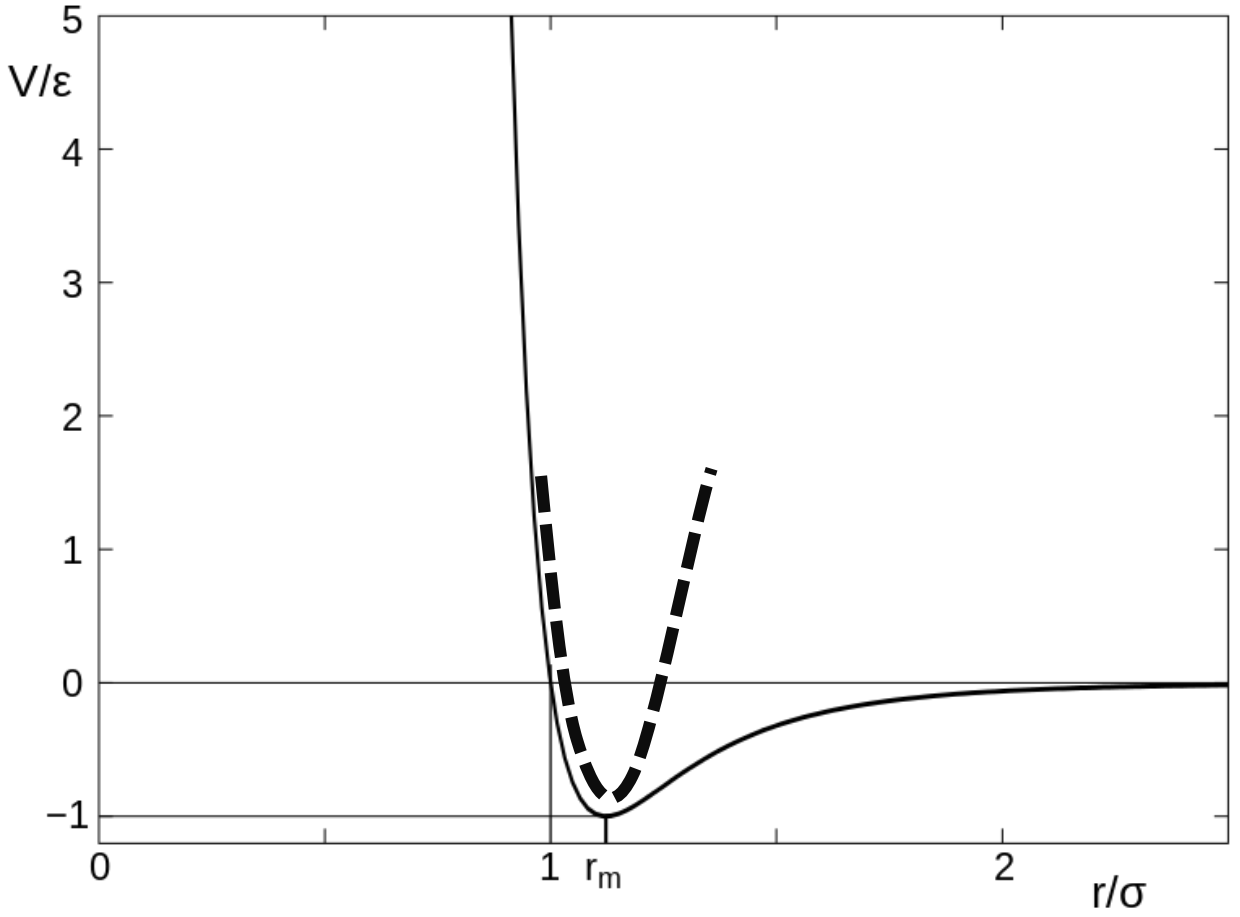

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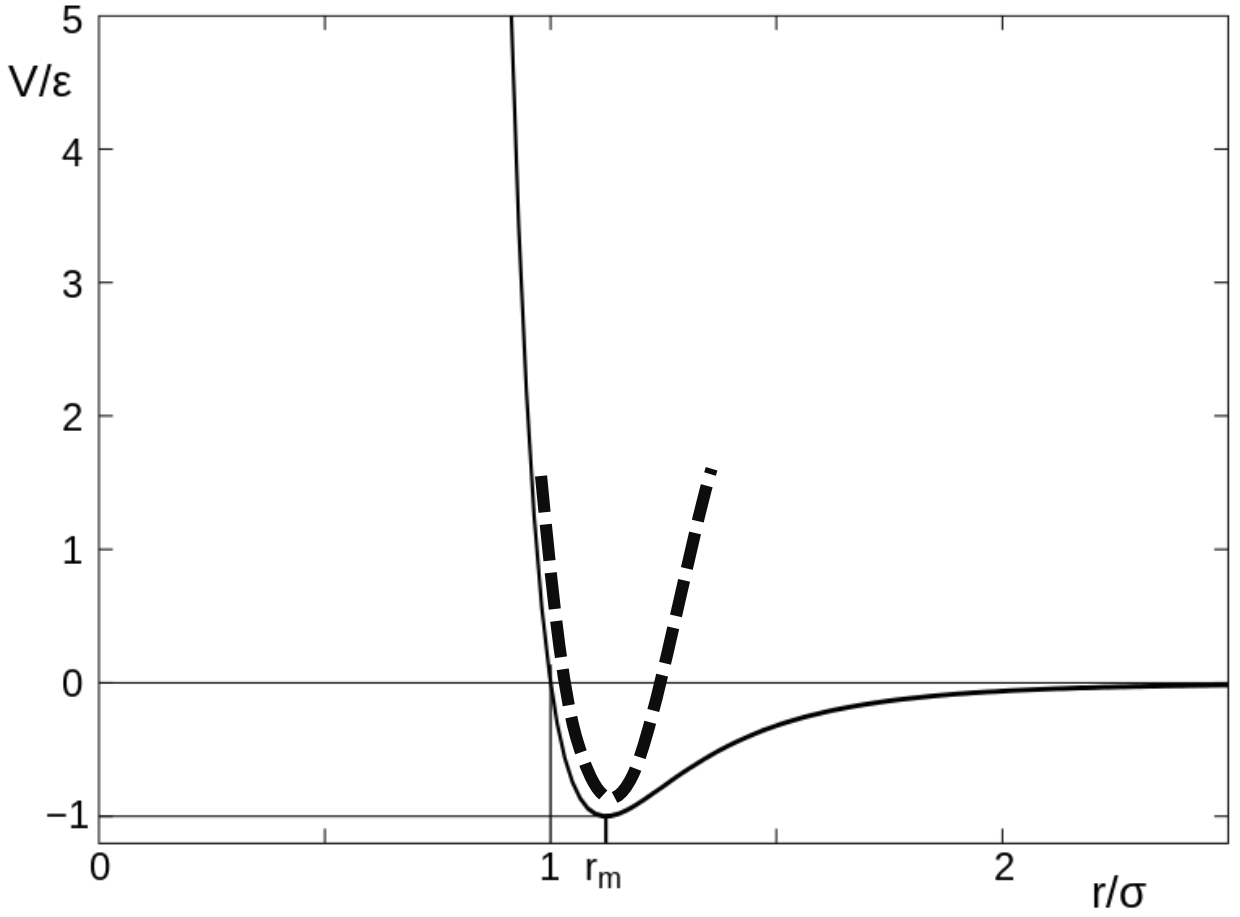

N_2 Gaussian calculation

- N_2 geometry optimization and vibrational frequency
  - Options: ground state, DFT, B3LYP, cc-pVTZ

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N_2 Gaussian calculation

Temperature	Pressure
298.15 K	1 Atm.

	Z	ln(Z)	E (KCal/Mol)	C_v (Cal/Mol-Kelvin)	S (Cal/Mol-Kelvin)
Electronic	1.000	0.000	0.000	0.000	0.000
Translational	0.583E+07	15.578	0.889	2.981	35.924
Rotational	51.266	3.937	0.592	1.987	9.811
Vibrational	1.000	0.007E-04	3.502	0.002	0.000
Total	0.299E+09	19.514	4.983	4.970	45.735
NIST source					45.7957 ± 0.001

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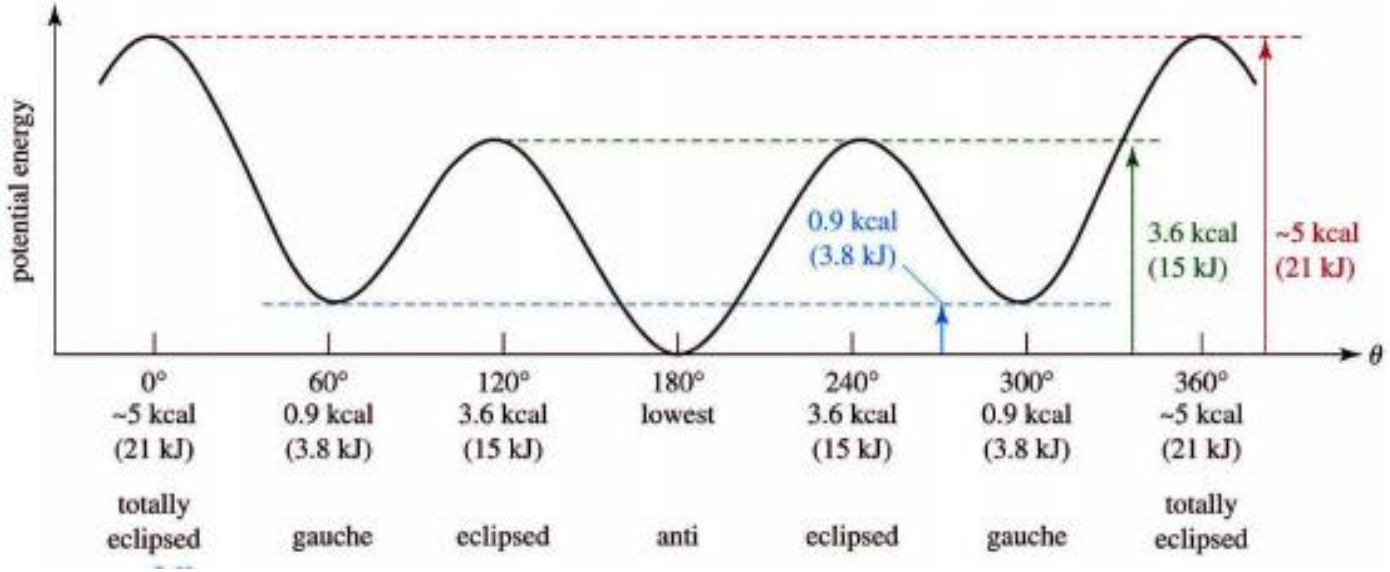
Limitations

- Systems in solution

Pes of 4 conformers of butane. Digital image. *Http://chemistry.stackexchange.com/*. N.p., 3 Oct. 2015. Web. 6 Apr. 2016. <http://i.stack.imgur.com/fgsHn.png>.

Limitations

- Systems in solution
- Molecules with many rotational conformers
  - Butane as shown below



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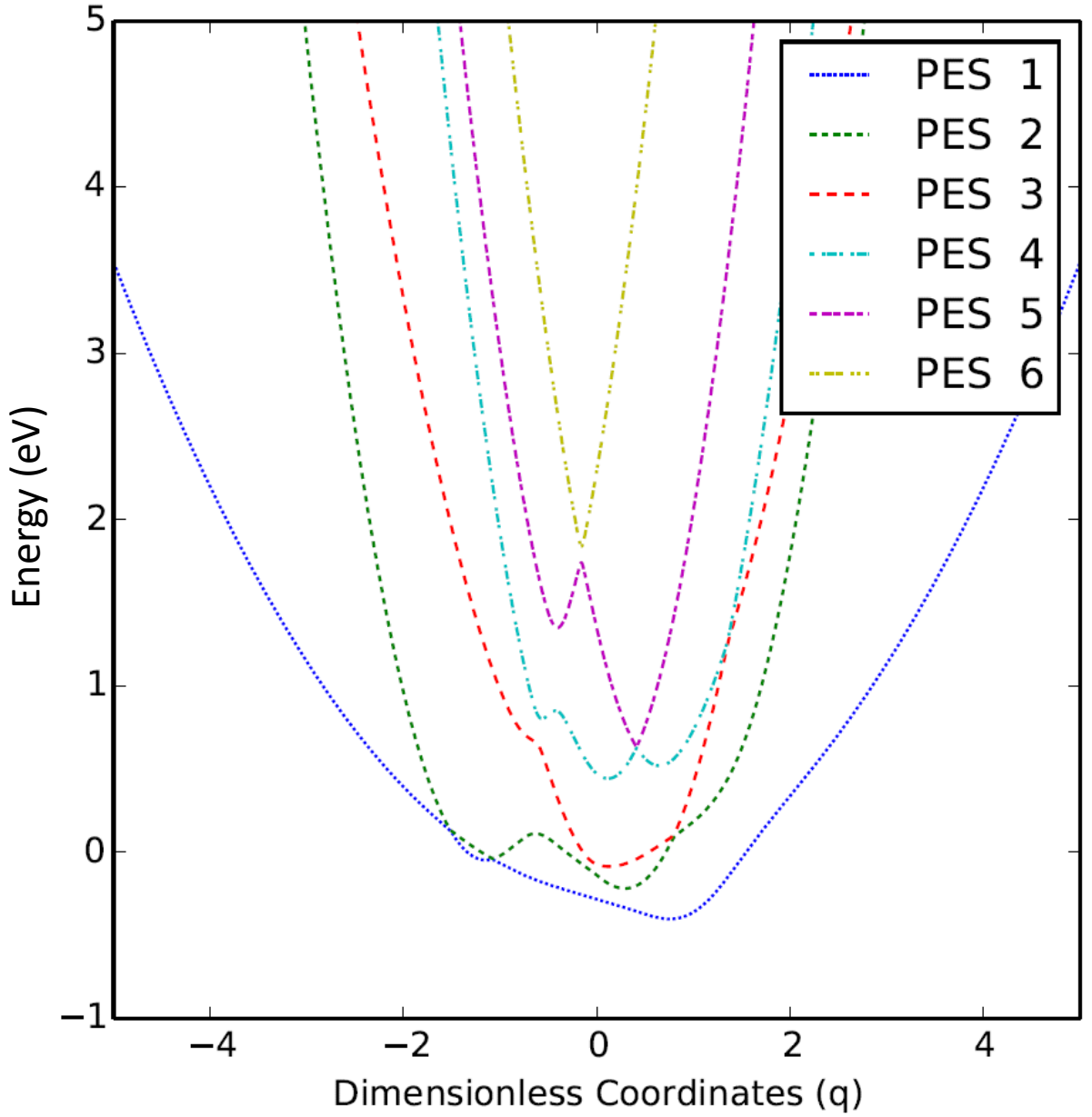
Nonadiabatic systems

Systems of interest have many low lying electronic surfaces

transition metal atoms, radicals



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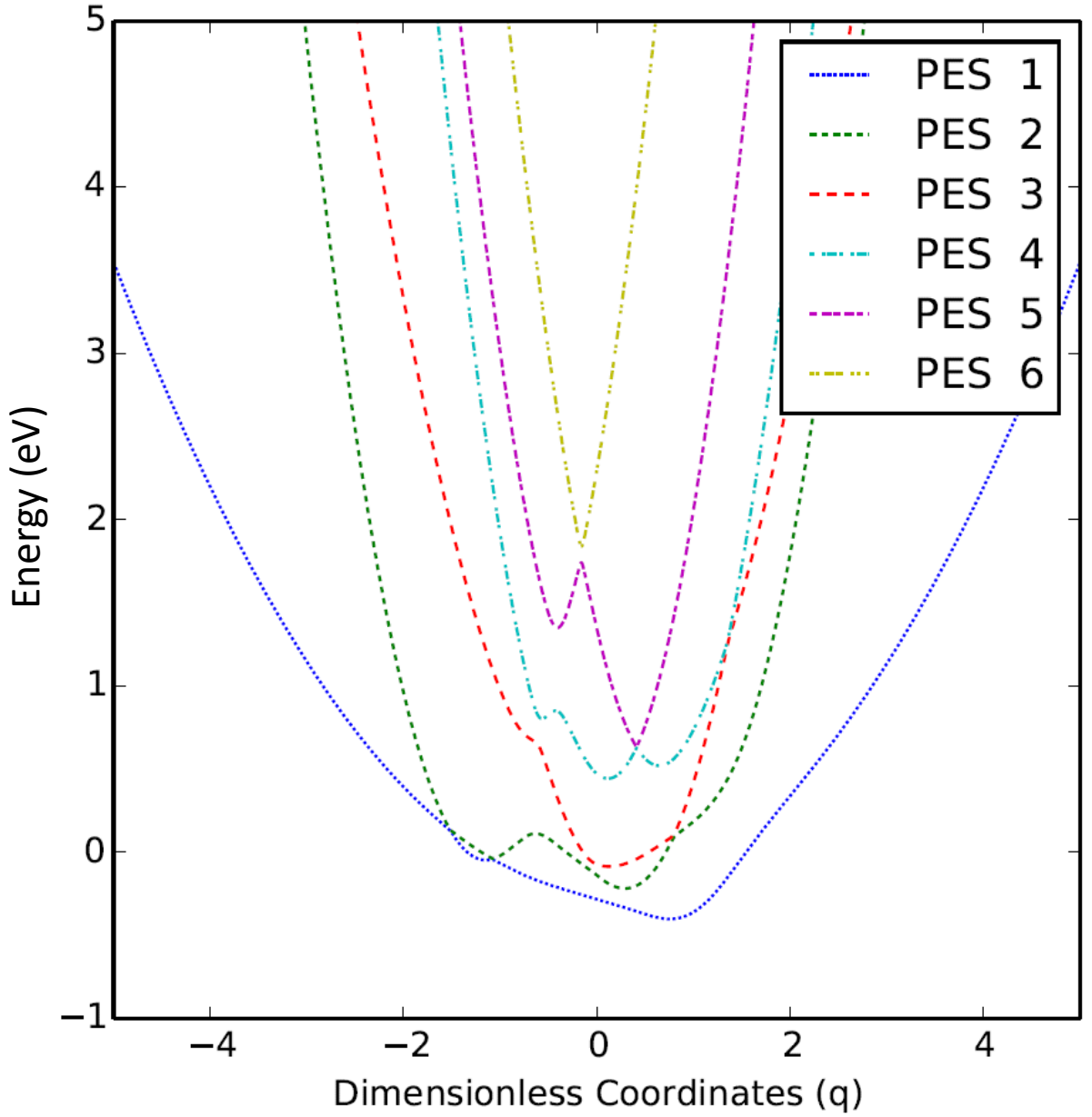

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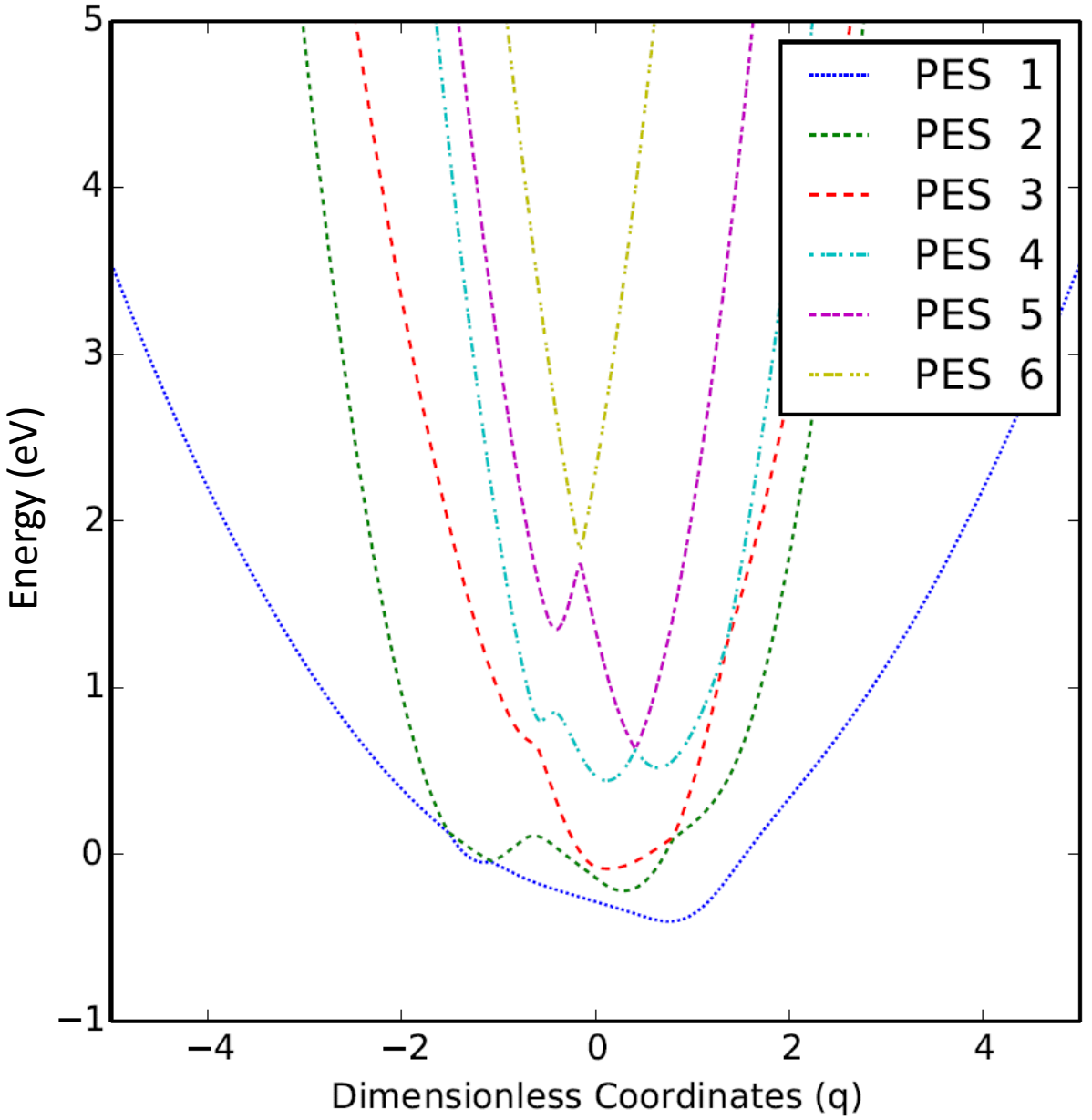

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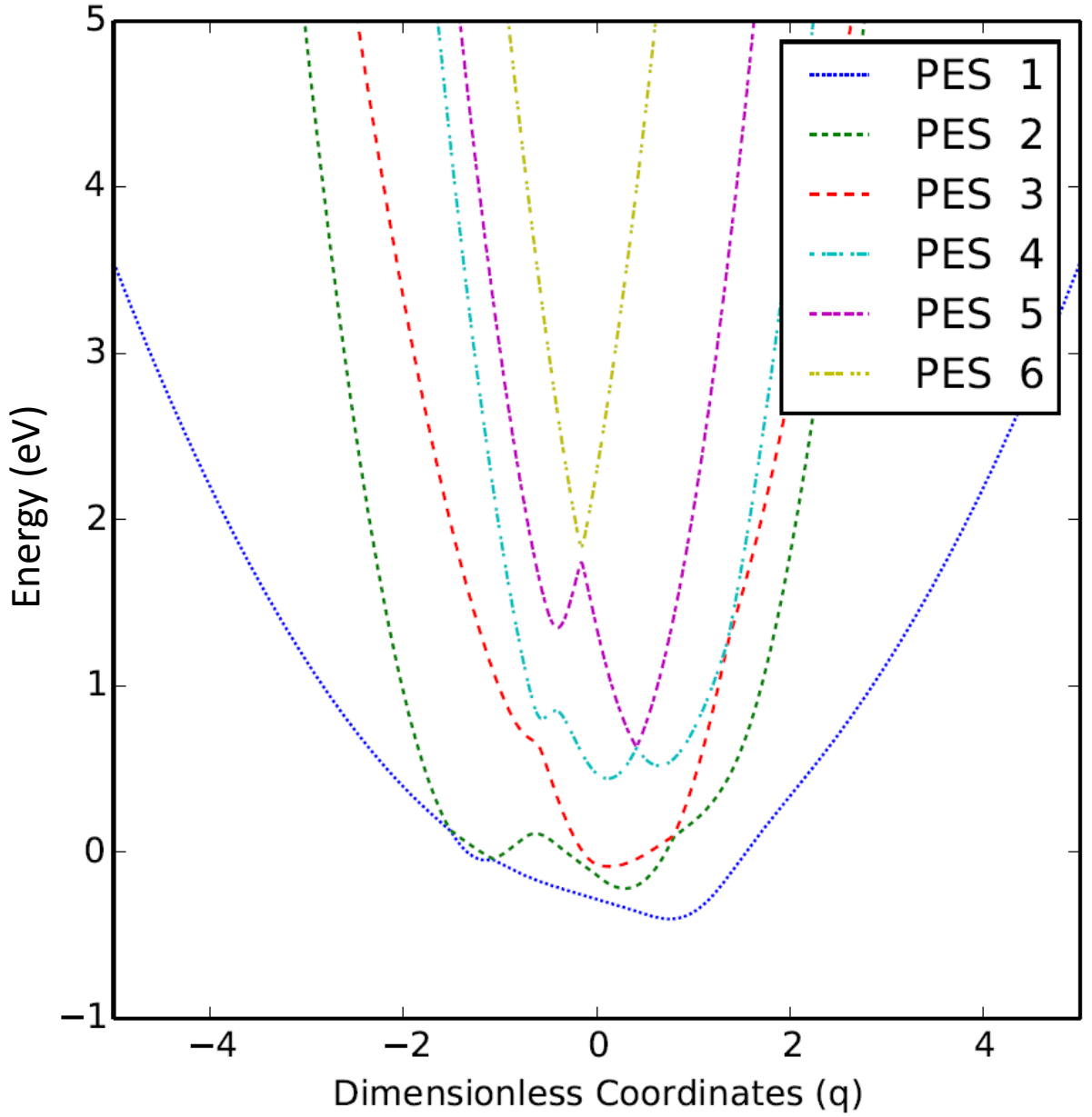

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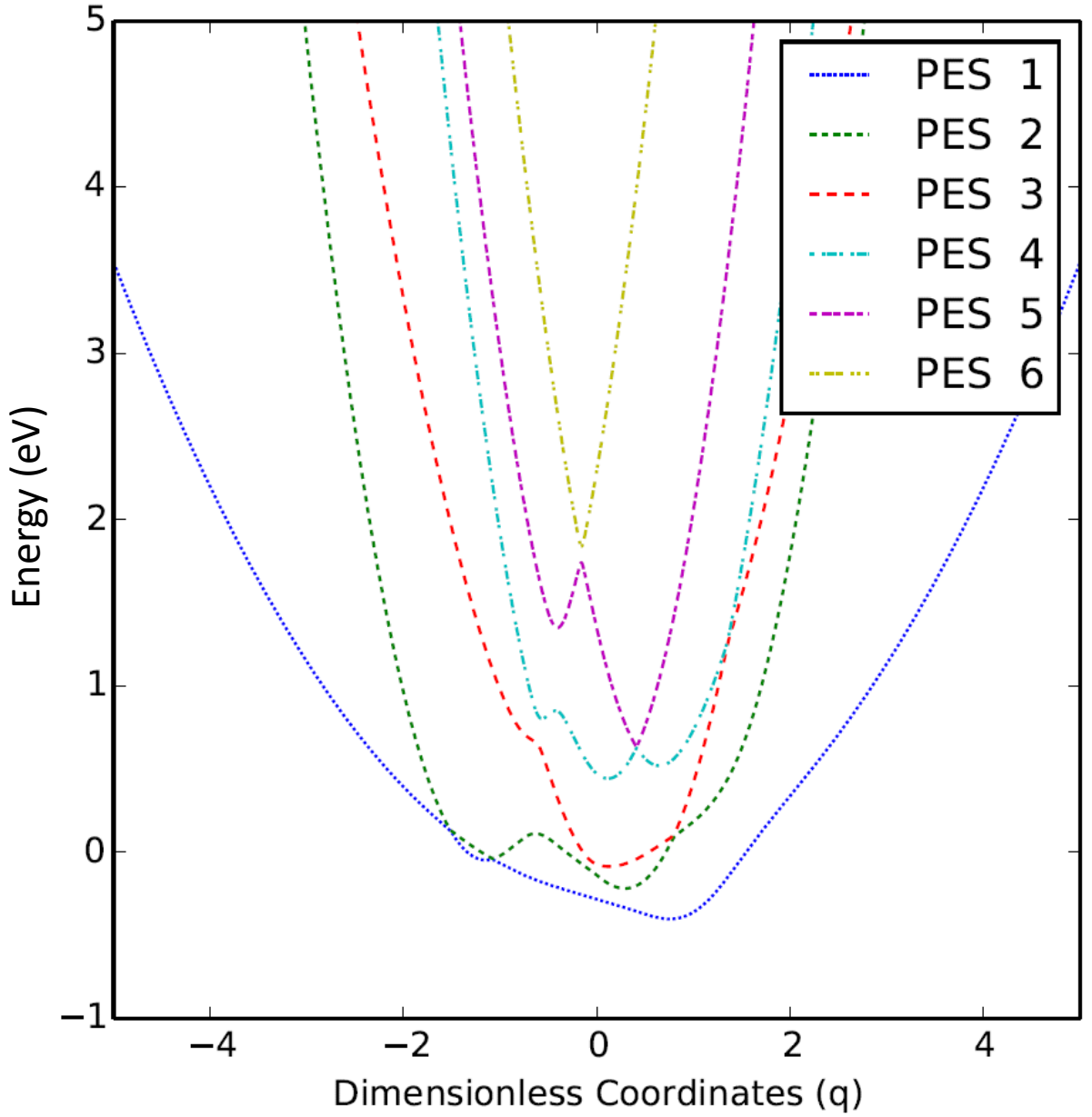

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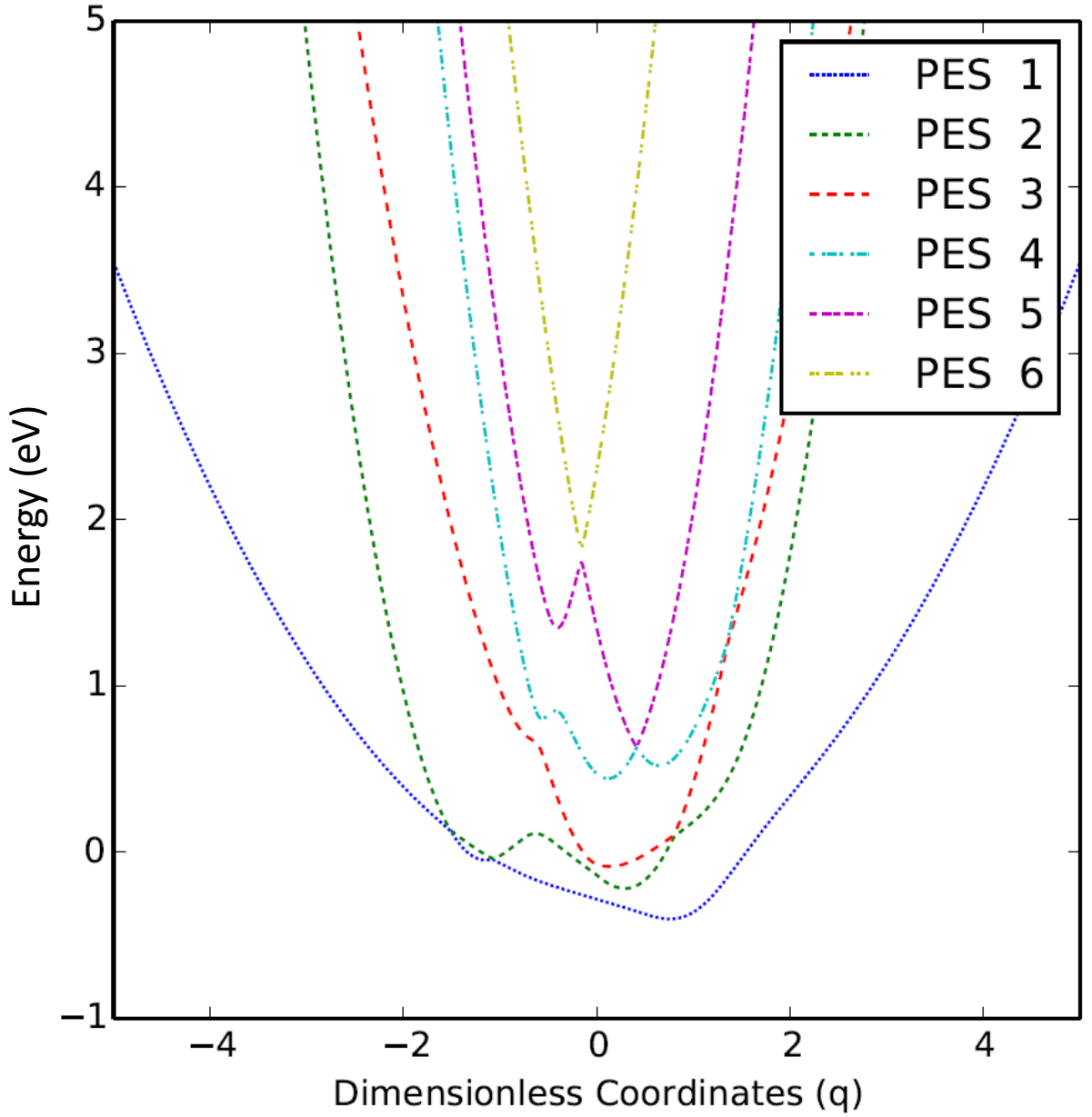

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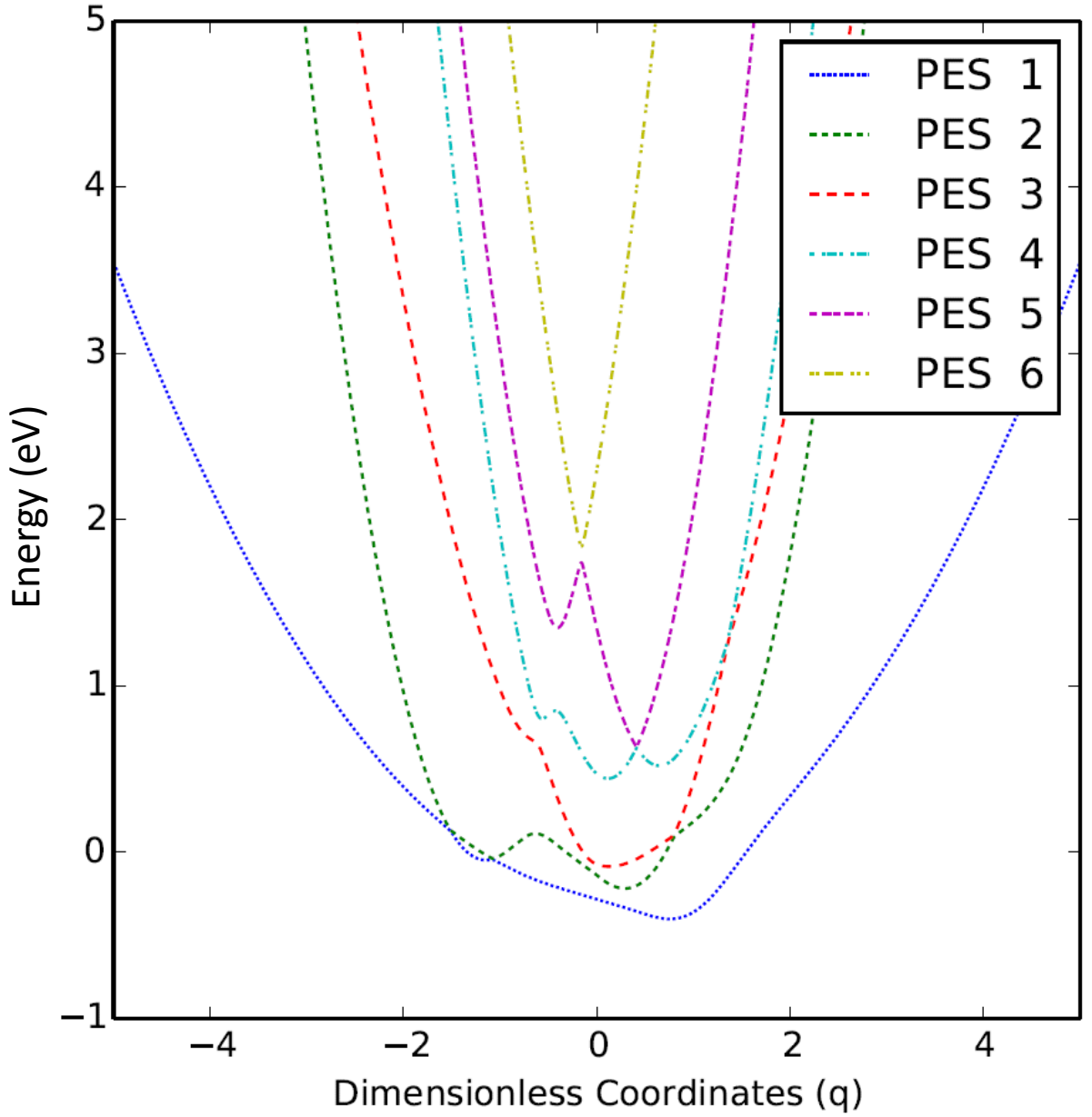

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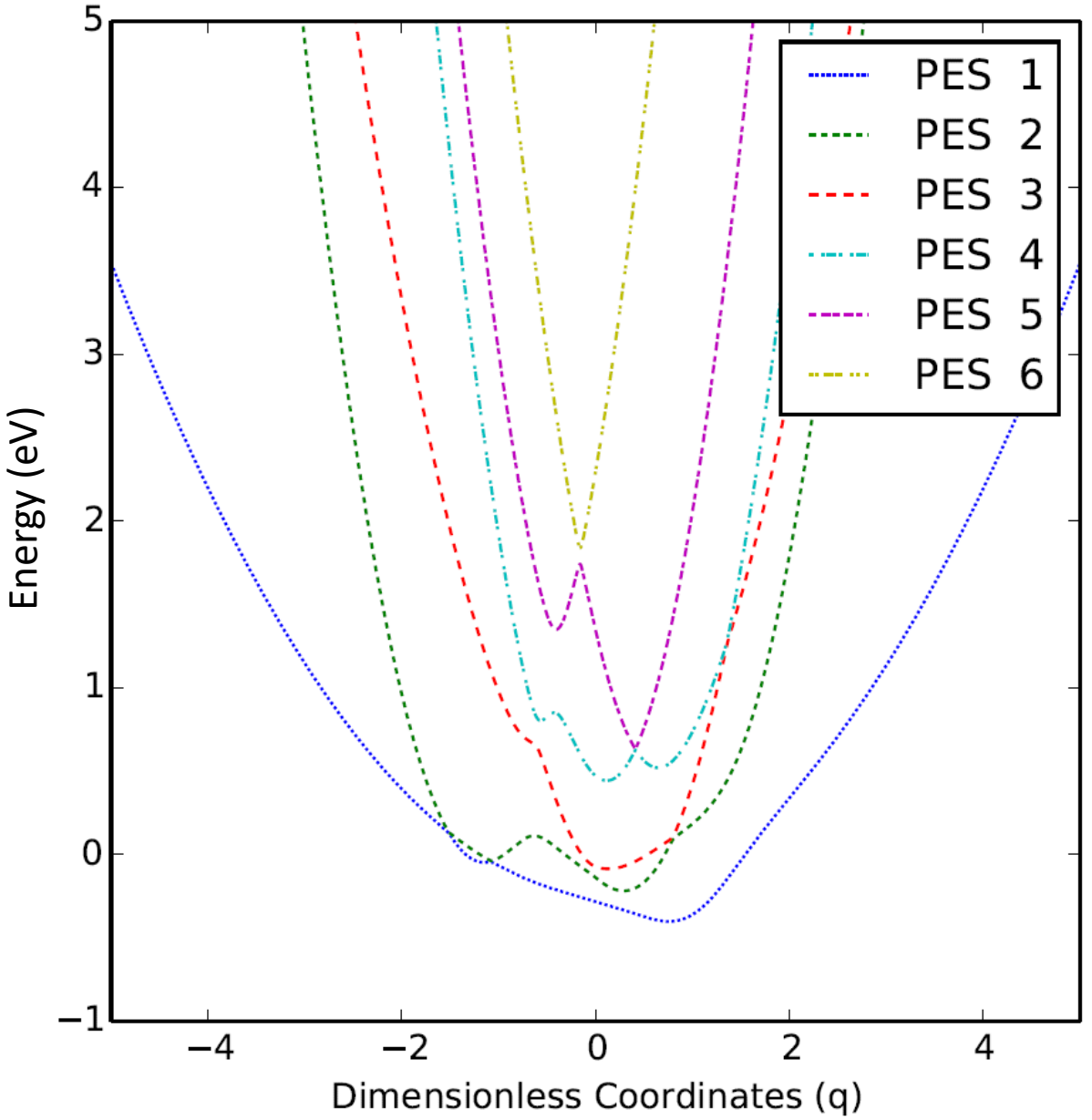

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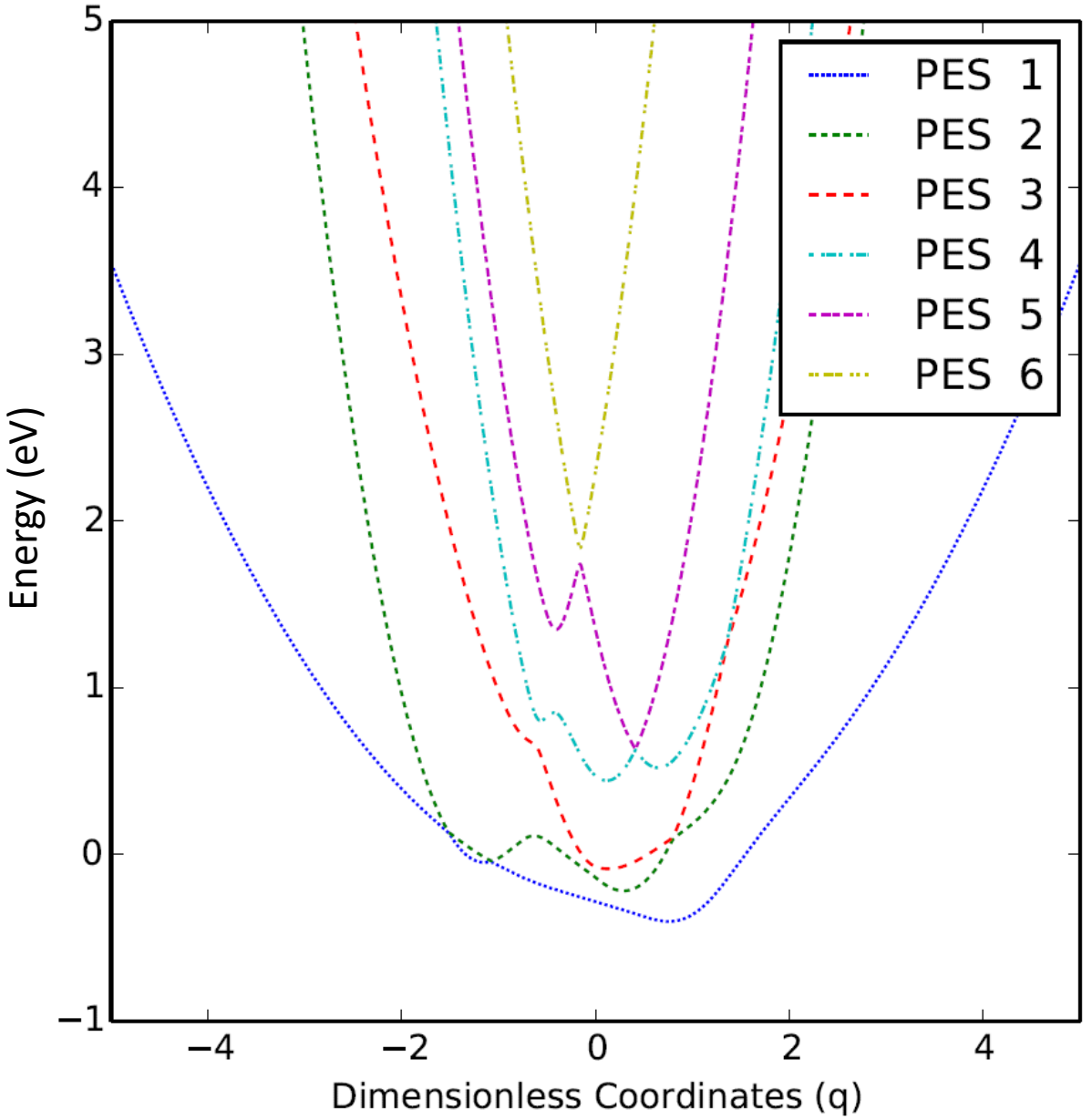
Vibronic Hamiltonian



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Electronic Hamiltonian

Nuclear & Electronic separation

$$\psi_{bo} = \underbrace{\phi(R)}_{\text{Nuclear}} \underbrace{\chi(r;R)}_{\text{Electonic}}$$

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$$\hat{H}\psi_{bo} = \left[\hat{T}_N(R) + \hat{V}_{NN}(R) + \hat{H}_e(r;R)\right]\phi(R)\chi(r;R)$$

Obtain electronic energies

$$\hat{H}_e(r;R)\chi_n(r;R)$$

$$= \left(\hat{T}_e(r) + \hat{V}_{ee}(r) + \hat{V}_{Ne}(r;R)\right)\chi_n(r;R)$$

$$= E_n(R)\chi_n(r;R)$$

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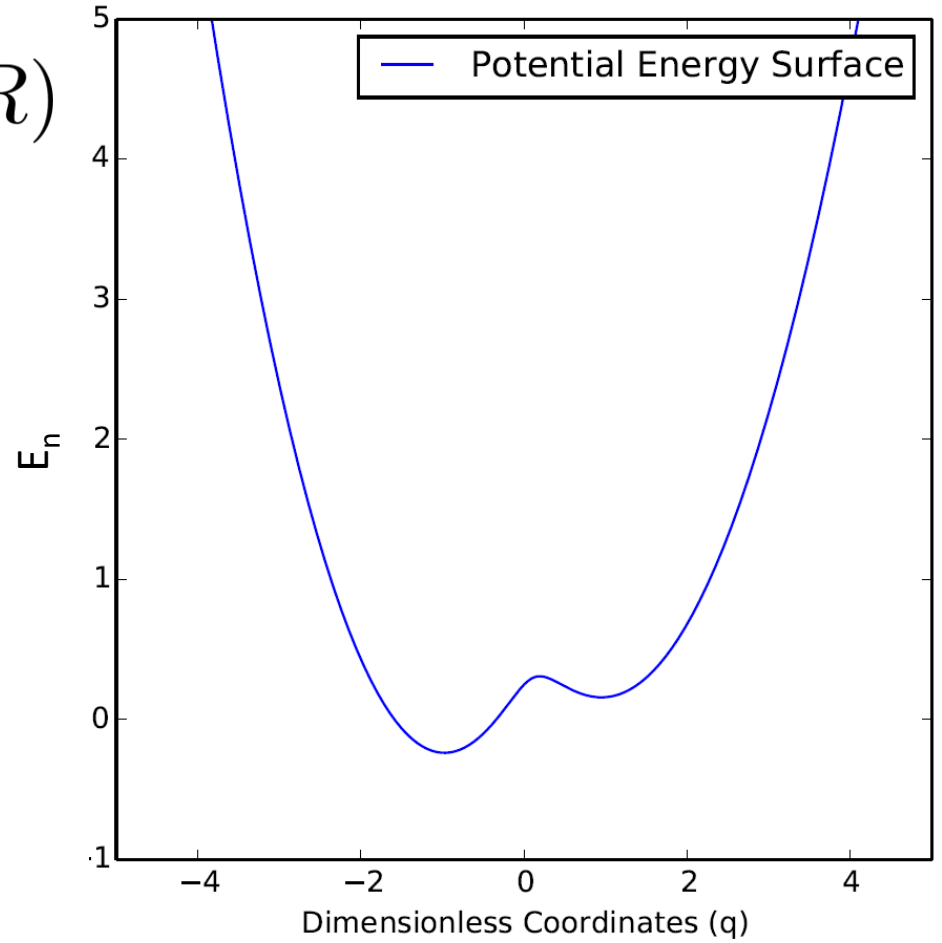

Solve for a given configuration R

$$\hat{H}\phi_n = \left[\hat{T}_N(R) + \underbrace{\hat{V}_{NN}(R) + E_e(R)}\right]\phi_n(R)$$

$$= \left[\hat{T}_N(R) + U_e(R)\right]\phi_n(R)$$

$$= E\phi_n$$

Terminology

$$\psi_{bo} = \underbrace{\phi(R)}_{\text{Nuclear}}\ \underbrace{\chi(r;R)}_{\text{Electonic}}$$

- Adiabatic $\hat{H} = \begin{pmatrix} \hat{T}_{11} & \hat{T}_{12} \\ \hat{T}_{21} & \hat{T}_{22} \end{pmatrix} + \begin{pmatrix} \hat{V}_{11} & 0 \\ 0 & \hat{V}_{22} \end{pmatrix}$ $\chi_A(r;R)$

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$$\chi_A(r;R)$$

Unitary Transformation

- Diabatic

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$$\chi_A(r;R)$$

Unitary Transformation

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$$\hat{H} = \begin{pmatrix} \hat{T}_{11} & 0 \\ 0 & \hat{T}_{22} \end{pmatrix} + \begin{pmatrix} \hat{V}'_{11} & \hat{V}_{12} \\ \hat{V}_{21} & \hat{V}'_{22} \end{pmatrix}$$

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$$\chi_D(r;R)$$

- Nonadiabatic
  - Systems with close or intersecting energy surfaces
  - Effects due to these off diagonal coupling terms

Examples of nonadiabatic effects

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- Drives essential parts of visible and ultraviolet photochemistry and photobiology

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- Collisions of electronically excited species

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- Chemiluminescent reactions

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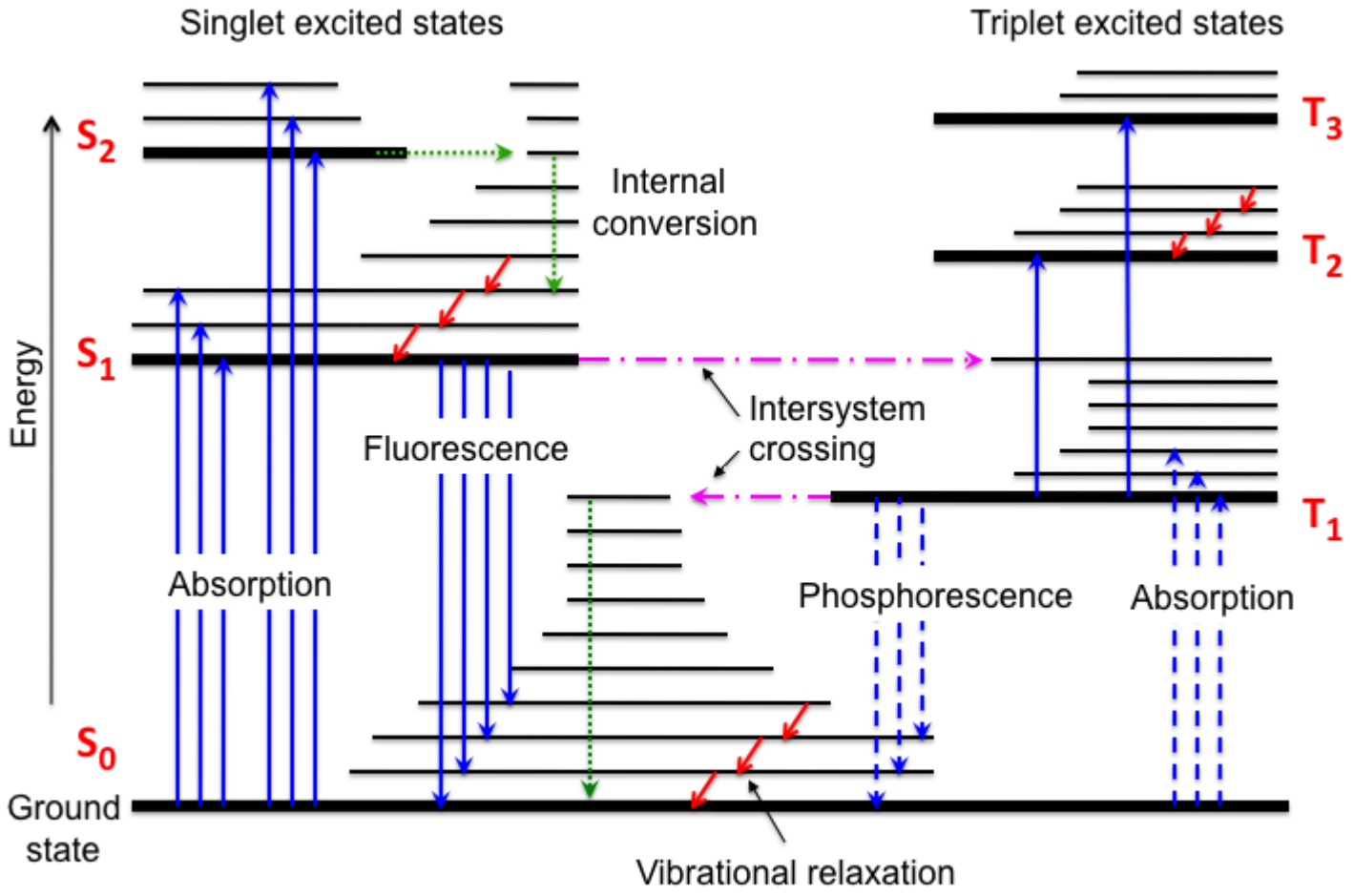
- Drives essential parts of visible and ultraviolet photochemistry and photobiology
- Collisions of electronically excited species
- Chemiluminescent reactions
- Electron transfer processes

Conical intersections and internal conversion

<u>Internal conversion</u>

Transition from higher to lower electronic state without emission of photons



http://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Spectroscopy/Electronic_Spectroscopy/Jablonski_diagram

Sobolewski, Andrzej L., and Wolfgang Domcke. "The chemical physics of the photostability of life." *Europhysics News* 37.4 (2006): 20-23.

Conical intersections and internal conversion

Conical intersection

Molecular Geometry point at which two potential energy surfaces are degenerate (intersect)

Suzuki, Toshinori. "Ultrafast Internal Conversion of Aromatic Molecules Studied by Photoelectron Spectroscopy using Sub-20 fs Laser Pulses." *Molecules* 19.2 (2014): 2410-2433.

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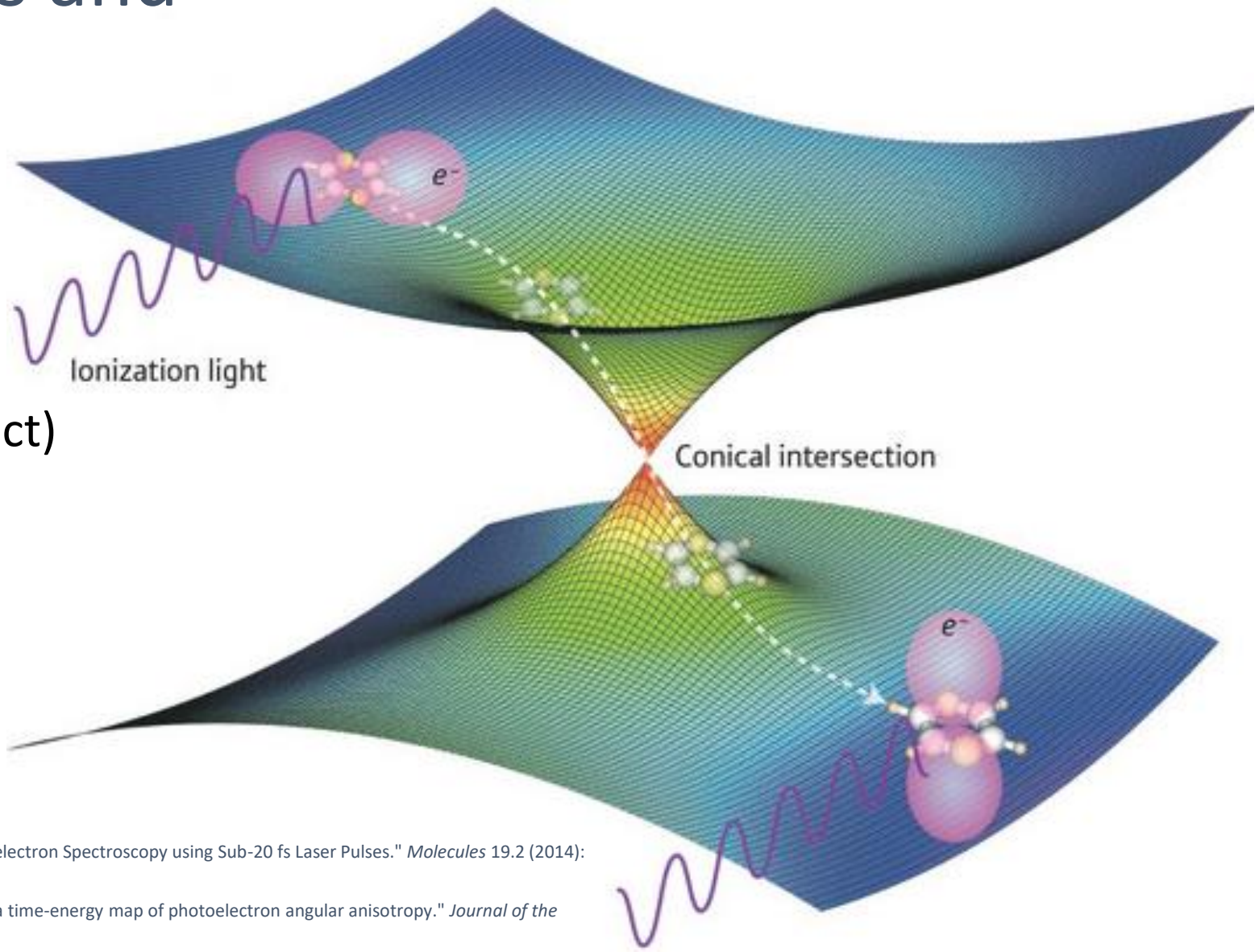

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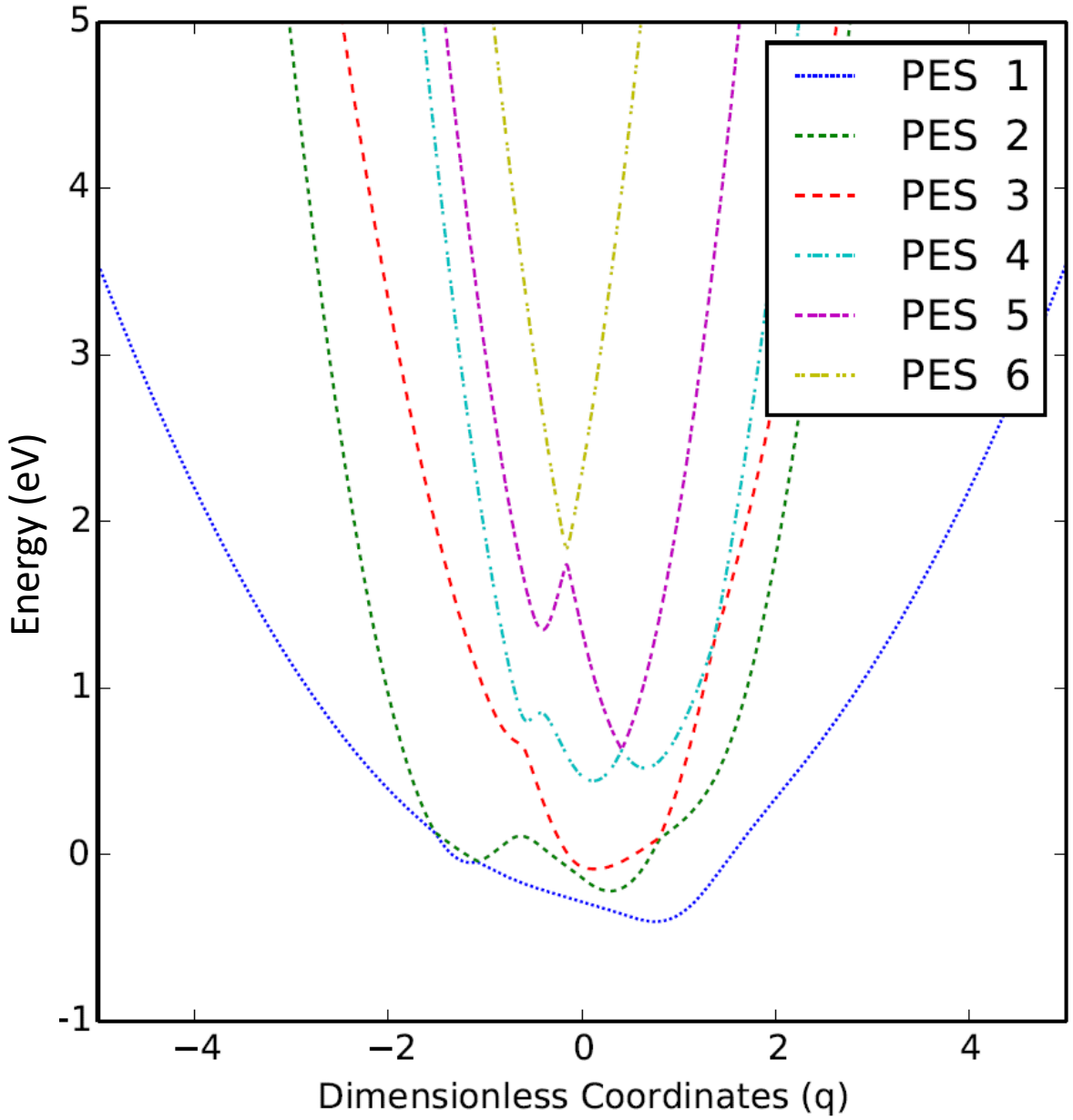
Nonadiabatic effects

- Most discussion is in terms of dynamics and relates to processes that occur over time
- Our focus is on thermodynamic properties of nonadiabatic systems in thermal equilibrium



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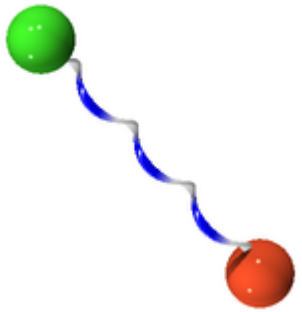

Feynman's Path Integrals

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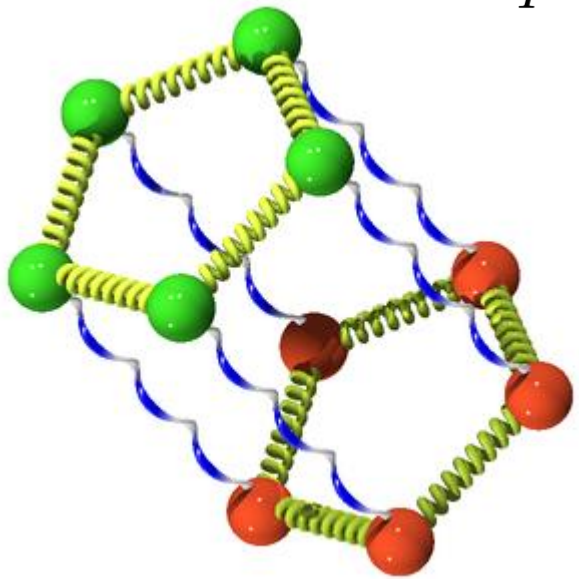
Classical limit $P = 1$

Quantum limit $\lim_{P \to \infty}$



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Structure of Hamiltonian - Trotter

- Re-express vibronic Hamiltonian

$$\hat{H}_{vib} = \hat{T}(\mathbf{R}) + \hat{U}(\mathbf{R})$$

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Analytical forms

- Probability distribution function of the system of interest

$$g\left(\{\mathbf{R}\}\right) = \mathrm{Tr}[\mathbb{O}(\mathbf{R}_1, \mathbf{R}_2)\mathbb{M}(\mathbf{R}_2)\mathbb{O}(\mathbf{R}_2, \mathbf{R}_3)\cdots\mathbb{O}(\mathbf{R}_P, \mathbf{R}_1)\mathbb{M}(\mathbf{R}_1)]$$

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Monte Carlo estimator

Expected value of function f(x) with normalized probability distribution function p(x)

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- We would like to sample from $\varrho(\{\mathbf{R}\})$

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$A = -k_B T \ln(Z)$	$C_v = \frac{1}{k_B T^2} \left(\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \left[\frac{-1}{Z} \frac{\partial Z}{\partial \beta} \right]^2 \right)$
$S = \frac{\partial}{\partial T} \left(k_B T \ln(Z) \right)$	$U = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln(Z)}{\partial \beta}$

Method 2: Coordinate scaling

$$Z(\beta') = \int \mathrm{d}q \, \varrho(q, \beta) \frac{g(q', \beta')}{\varrho(q', \beta')}$$

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$$\frac{\partial Z(\beta')}{\partial \beta'} = \int \mathrm{d}q\, \varrho(q,\beta) \frac{\partial}{\partial \beta'} \left[f(q',\beta') \Big|_{\beta'=\beta} \right.$$

$$= \int \mathrm{d}q\, \varrho(q,\beta) \frac{1}{2\Delta\beta} \Big[f(q',\beta+\Delta\beta) - f(q',\beta-\Delta\beta) \Big]$$

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$A = \langle e \rangle_g - T \left[\int_0^{T_f} \frac{\langle c \rangle_g}{T} \mathrm{d}T \right]$	$C_v = \langle c \rangle_g = \frac{\langle cw \rangle_\varrho}{\langle w \rangle_\varrho}$
$S = \int_0^{T_f} \frac{C_v}{T} \mathrm{d}T$	$U = \langle e \rangle_g = \frac{\langle ew \rangle_\varrho}{\langle w \rangle_\varrho}$

Sum over states method

Armadillo C++ template library

$$Z = \sum_n e^{-\beta E_n}$$

$A = U - TS$	$C_v = \frac{1}{k_B T^2}\left(\sum_n E_n^2 \frac{e^{-\beta E_n}}{Z} - U^2\right)$
$U = \frac{1}{Z}\sum_n E_n e^{-\beta E_n}$	$S = -\frac{k_B}{Z}\sum_n e^{-\beta E_n}\ln(p_n)$

Sum over states method

- Vibronic Hamiltonian (with coupling)

$$\begin{bmatrix} E_1 + \frac{1}{2}\omega_1 (q - q_{m1})^2 & \mu q & \mu q & \mu q & \mu q \\ \mu q & E_2 + \frac{1}{2}\omega_2 (q - q_{m2})^2 & \mu q & \mu q & \mu q \\ \mu q & \mu q & E_3 + \frac{1}{2}\omega_3 (q - q_{m3})^2 & \mu q & \mu q \\ \mu q & \mu q & \mu q & E_4 + \frac{1}{2}\omega_4 (q - q_{m4})^2 & \mu q \\ \mu q & \mu q & \mu q & \mu q & E_5 + \frac{1}{2}\omega_5 (q - q_{m5})^2 \end{bmatrix}$$

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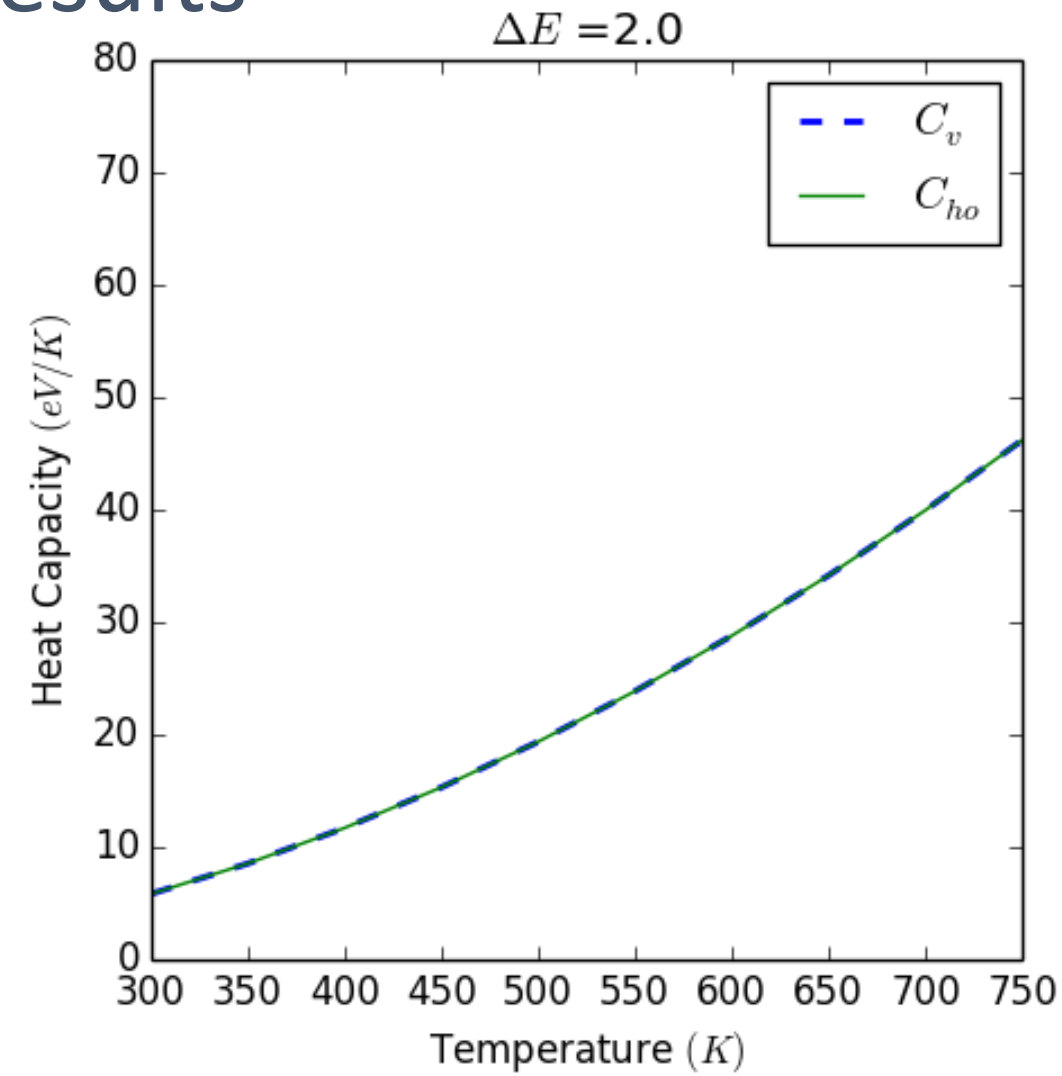
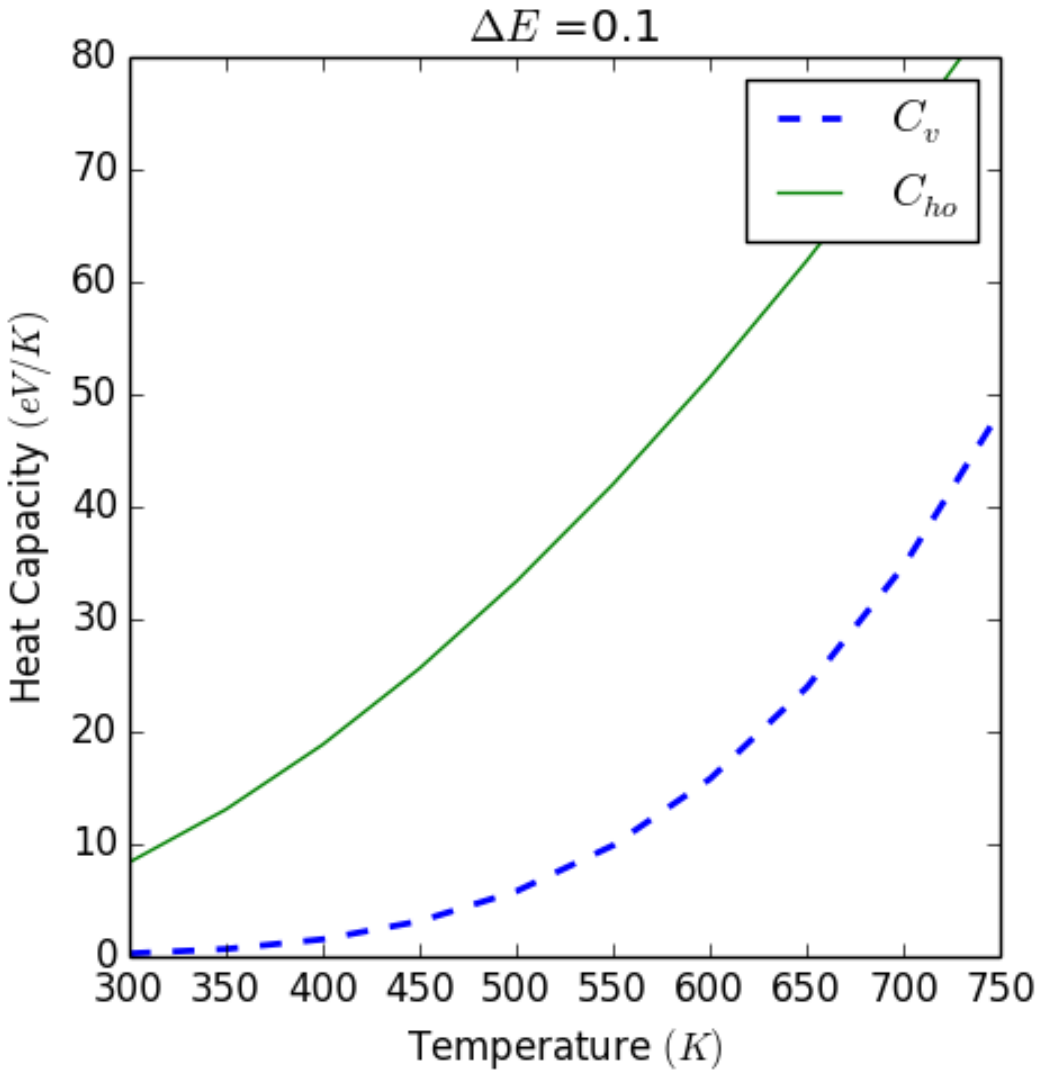
- Harmonic Hamiltonian (without coupling)

$$\begin{bmatrix} E_1 + \frac{1}{2}\omega_1 (q - q_{m1})^2 & 0 & 0 & 0 & 0 \\ 0 & E_2 + \frac{1}{2}\omega_2 (q - q_{m2})^2 & 0 & 0 & 0 \\ 0 & 0 & E_3 + \frac{1}{2}\omega_3 (q - q_{m3})^2 & 0 & 0 \\ 0 & 0 & 0 & E_4 + \frac{1}{2}\omega_4 (q - q_{m4})^2 & 0 \\ 0 & 0 & 0 & 0 & E_5 + \frac{1}{2}\omega_5 (q - q_{m5})^2 \end{bmatrix}$$

Results


ΔE =2.0
C_v
C_{ho}
Heat Capacity (eV/K)
Temperature (K)
0
10
20
30
40
50
60
70
80
300
350
400
450
500
550
600
650
700
750


ΔE =0.1
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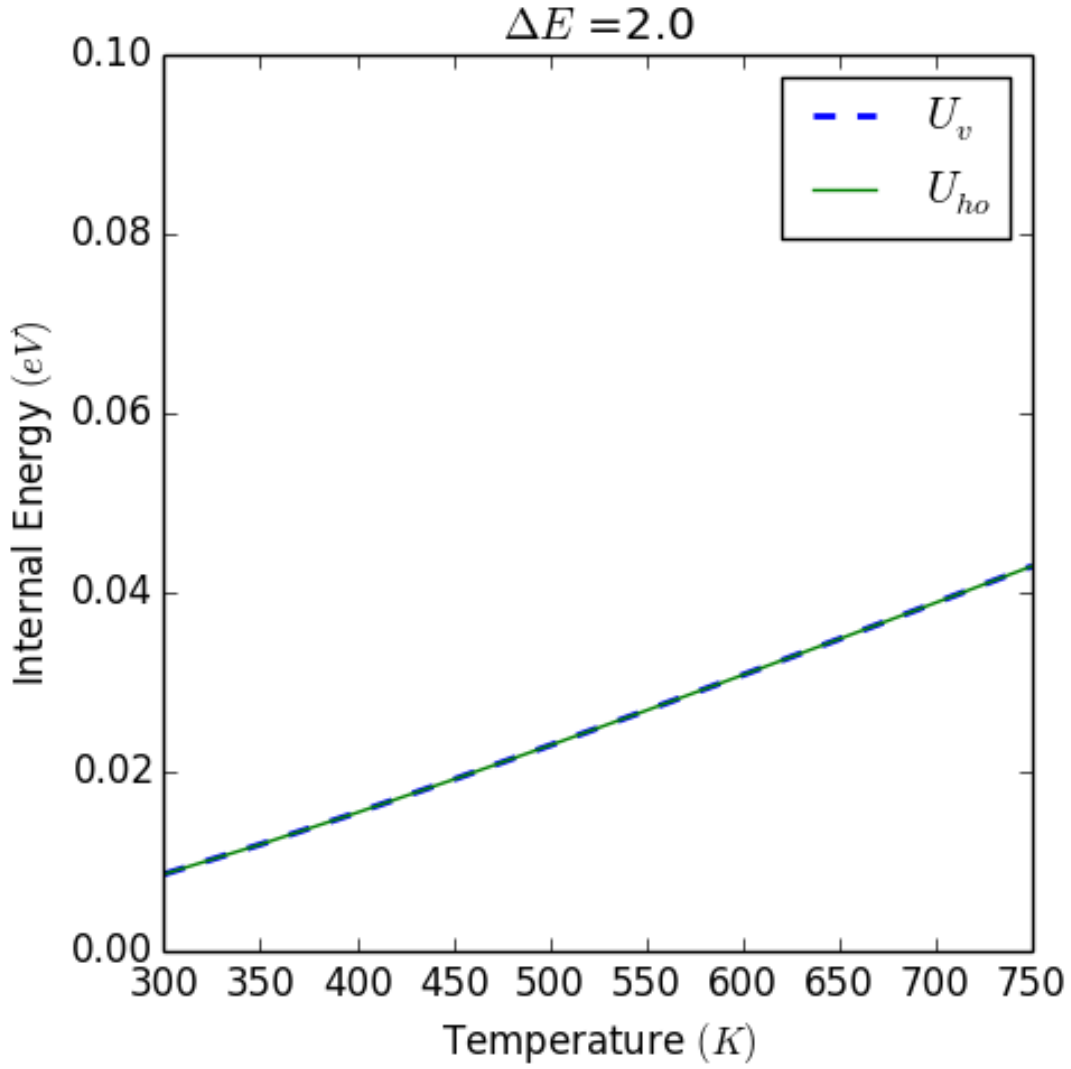
ΔE =2.0
0.10
0.08
0.06
0.04
0.02
0.00
Internal Energy (eV)
300 350 400 450 500 550 600 650 700 750
Temperature (K)
U_v
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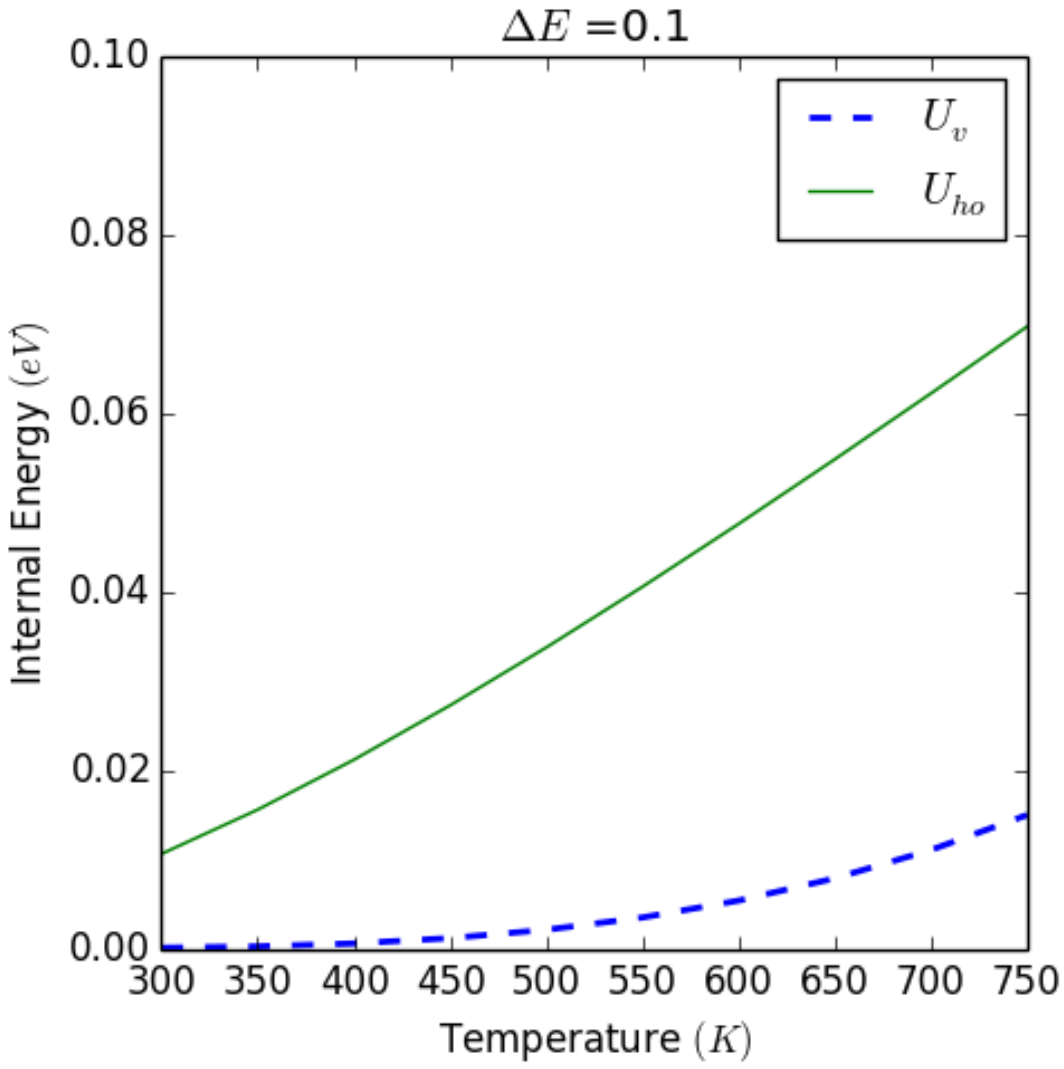
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- Completed PI python script for uncoupled system

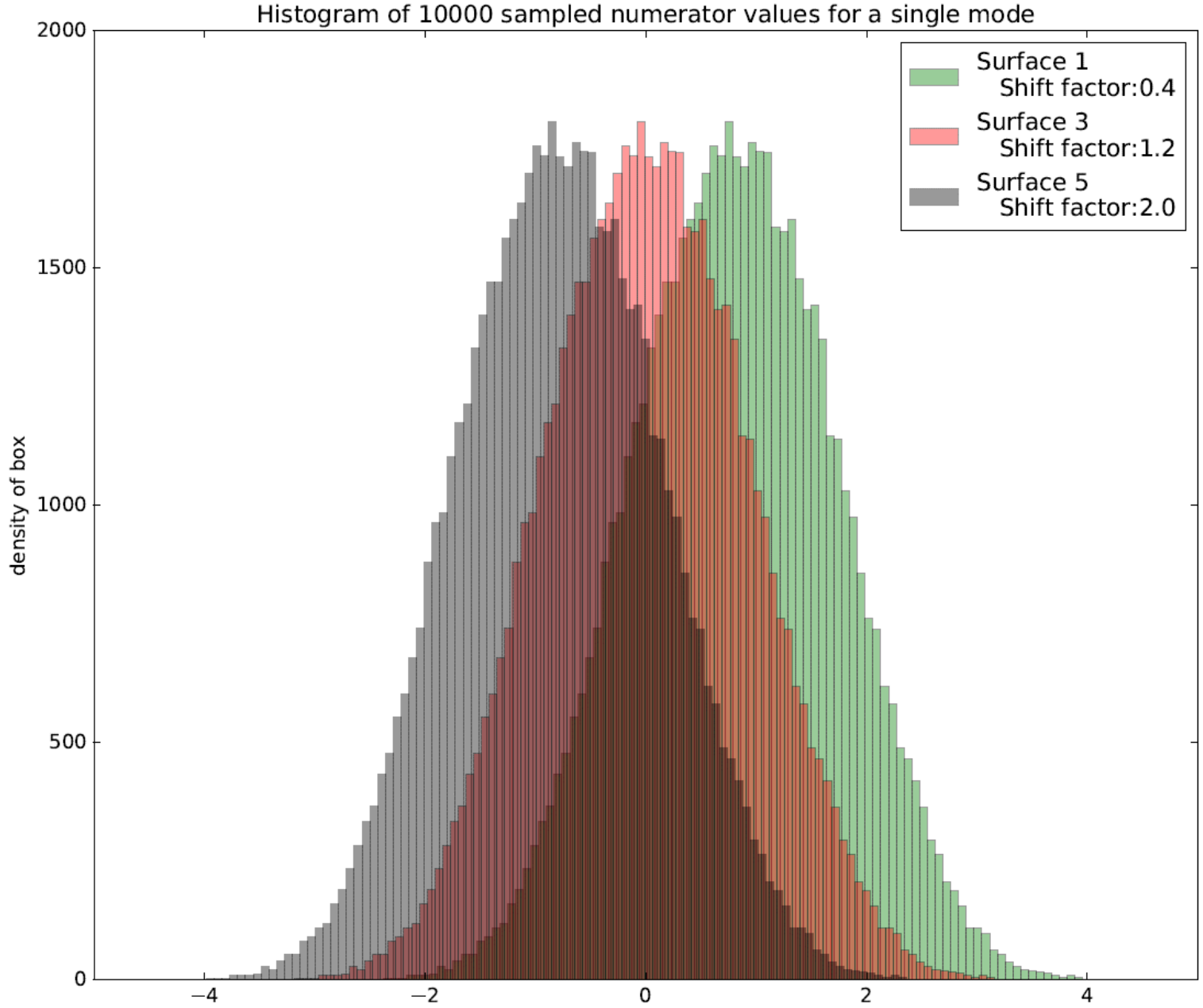
$$Z = \left\langle \frac{g\left(\{\mathbf{R}\}\right)}{\varrho\left(\{\mathbf{R}\}\right)} \right\rangle_{\varrho} \left(\int \mathrm{d}\left\{\mathbf{R}_{\gamma}\right\} \varrho\left(\{\mathbf{R}\}\right) \right)$$

$$g\left(\{\mathbf{R}\}\right) = \mathrm{Tr}[\mathbb{O}(\mathbf{R}_1, \mathbf{R}_2)\mathbb{M}(\mathbf{R}_2)\mathbb{O}(\mathbf{R}_2, \mathbf{R}_3) \cdots \mathbb{O}(\mathbf{R}_P, \mathbf{R}_1)\mathbb{M}(\mathbf{R}_1)]$$

$$\varrho\left(\{\mathbf{R}\}\right) = \mathrm{Tr}[\mathbb{O}(\mathbf{R}_1, \mathbf{R}_2)\mathbb{O}(\mathbf{R}_2, \mathbf{R}_3) \cdots \mathbb{O}(\mathbf{R}_P, \mathbf{R}_1)]$$

Current Progress

$$\left\langle \frac{g\left(\{\mathbf{R}\}\right)}{\varrho\left(\{\mathbf{R}\}\right)} \right\rangle_{\varrho}$$



Future

- Implement support for arbitrary coupling propagator $[\mathbb{M}(\mathbf{R}_{i+1})]_{n_i,n_{i+1}}$
- Implement quadratic and linear terms in SOS/analytical code(*correctly)
- Implement analytic portion of Z calculation $\left(\int \mathrm{d}\{\mathbf{R}_\gamma\}\, \varrho(\{\mathbf{R}\})\right)$
- Replicate the Python code in Fortran for increased performance

Conclusions

- Developed a path integral formulation for nonadiabatic systems
- Developed two approaches to calculating Z
- Derived estimators for thermodynamic properties
- About to start testing convergence of Path Integral Code