VIBRATIONAL RELAXATION OF *NO* SCATTERING FROM *AU*(111)

VISTA Seminar

6th March 2024

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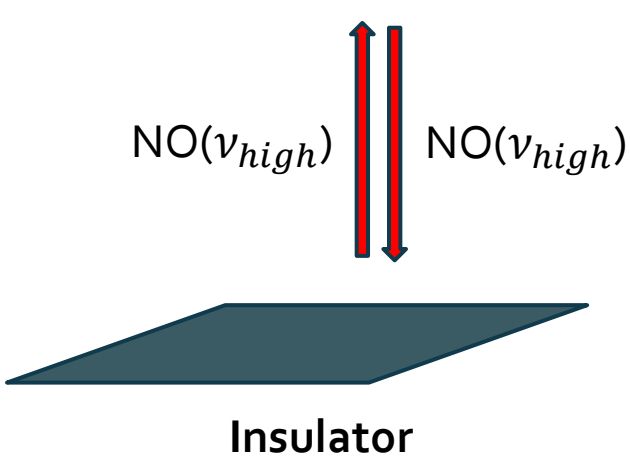
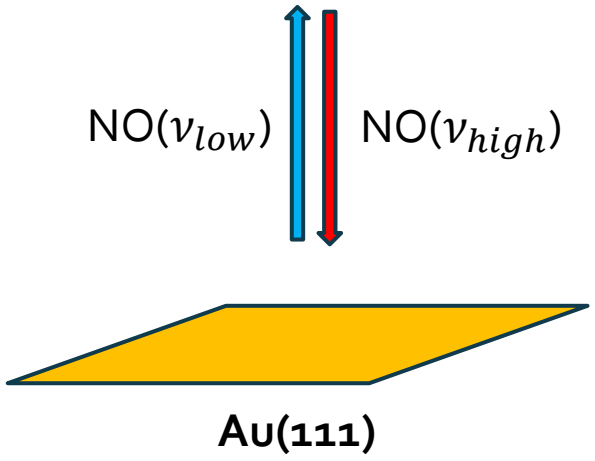
Ananth Group

Cornell University

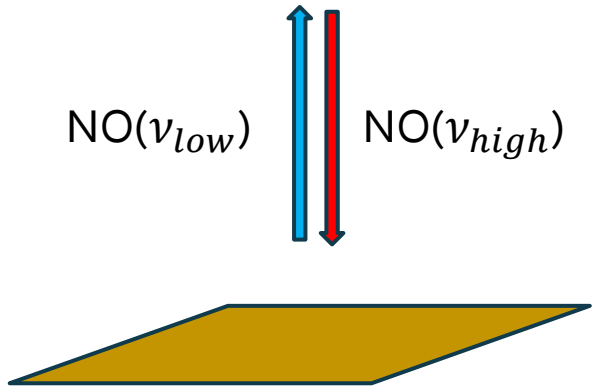
NO scattering from Au(111)



Insulator



Au(111)



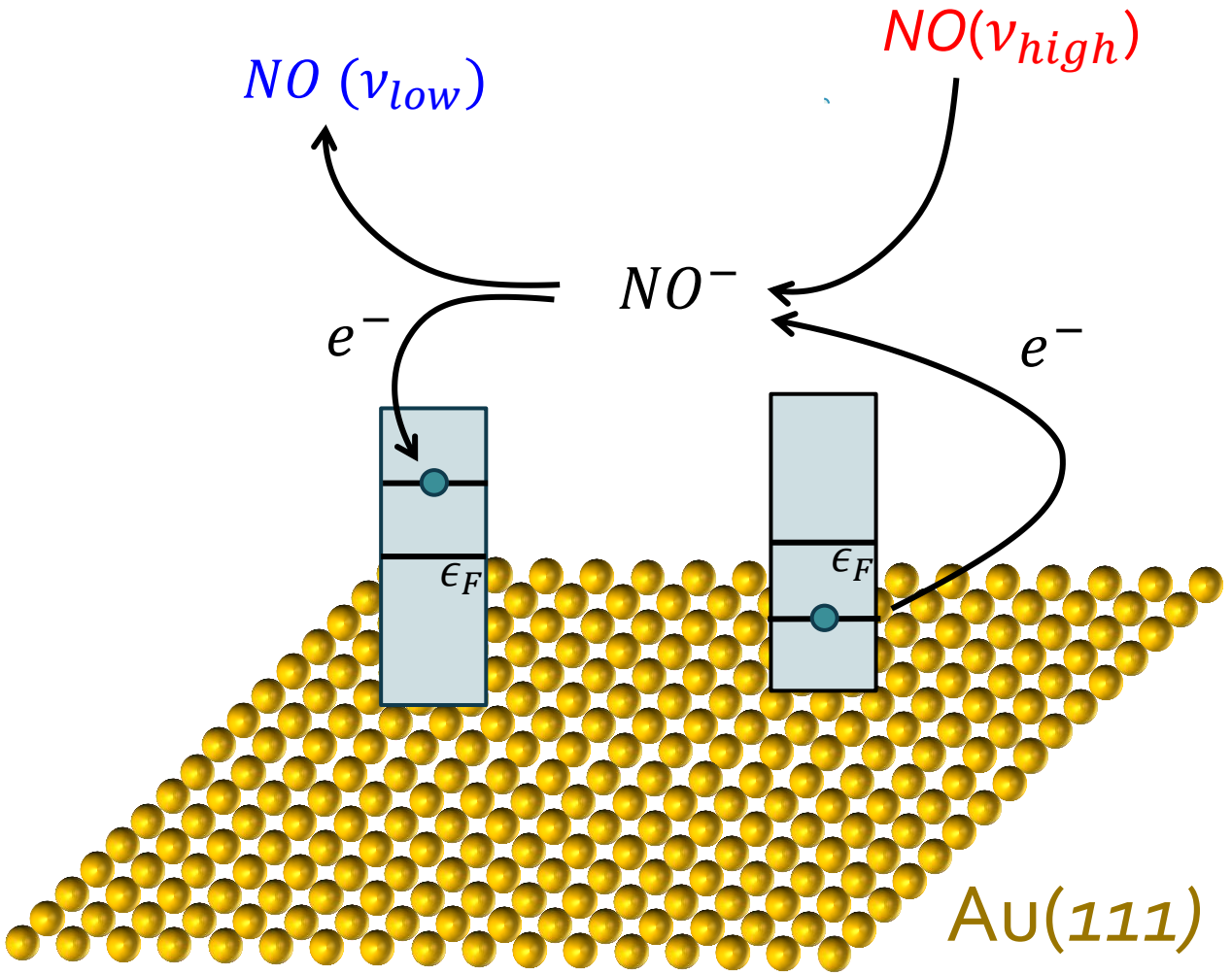
Electrons ejected from surface

Cs coated Au(111)

- K. Golibrzuch et. al., *Ann. Rev. Phys. Chem.*, **66,** 399 (2015)

Proposed mechanism

Vibrational energy is lost into electron hole pair excitations



- K. Golibrzuch et. al., *Ann. Rev. Phys. Chem.*, **66,** 399 (2015)

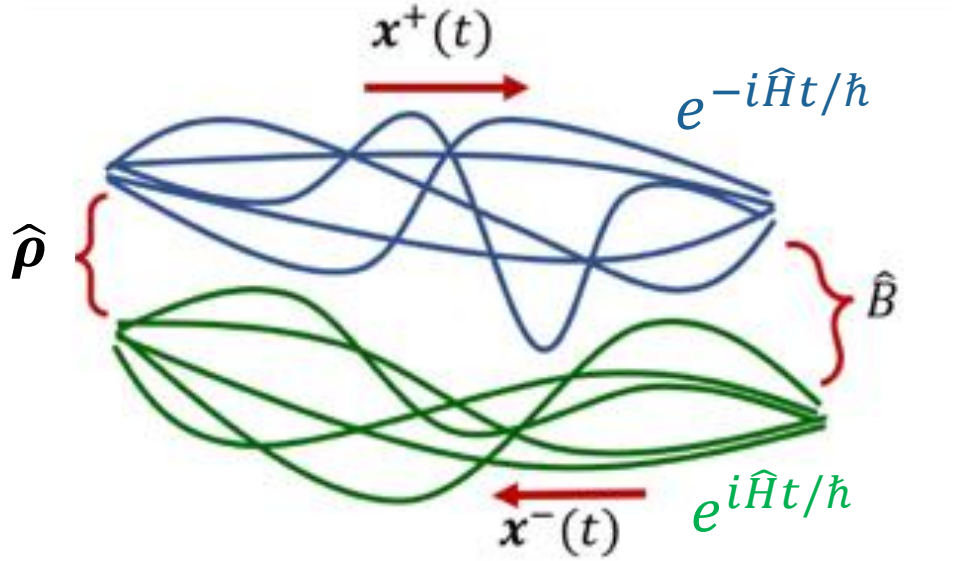
Prominent simulation approaches

- Independent Electron Surface Hopping (IESH)[1]
- Molecular Dynamics with Electronic Friction (MDEF)[2]
- Semiclassical Dynamics?

- [1] Shenvi et.al. *J. Chem. Phys.* ,130,174107 (2009)
- [2] Head-Gordon & Tully, *J. Chem. Phys.*, 103, 10137 (1995)

Quantum dynamics with path integrals

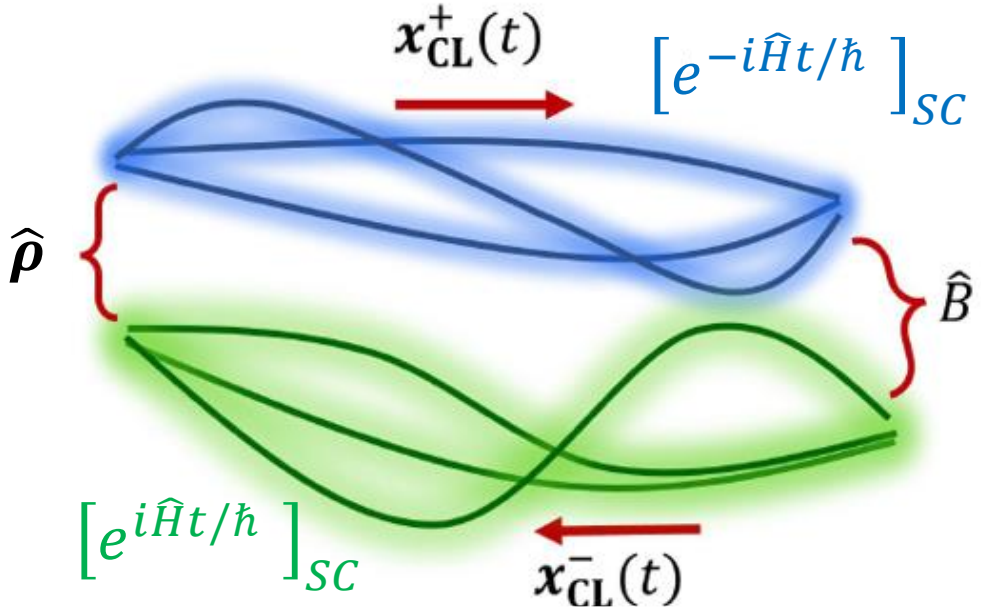
$$\langle \hat{B}(t) \rangle = Tr\left[\hat{\rho}\hat{B}(t)\right] = Tr\left[\hat{\rho} e^{i\hat{H}t/\hbar}\ \hat{B} e^{-i\hat{H}t/\hbar}\ \right]$$



- Count ***ALL*** forward and backward paths
- Weight them by their action: $e^{i(S^+ - S^-)/\hbar}$

-Quantum Mechanics and Path Integrals, Feynman & Hibbs

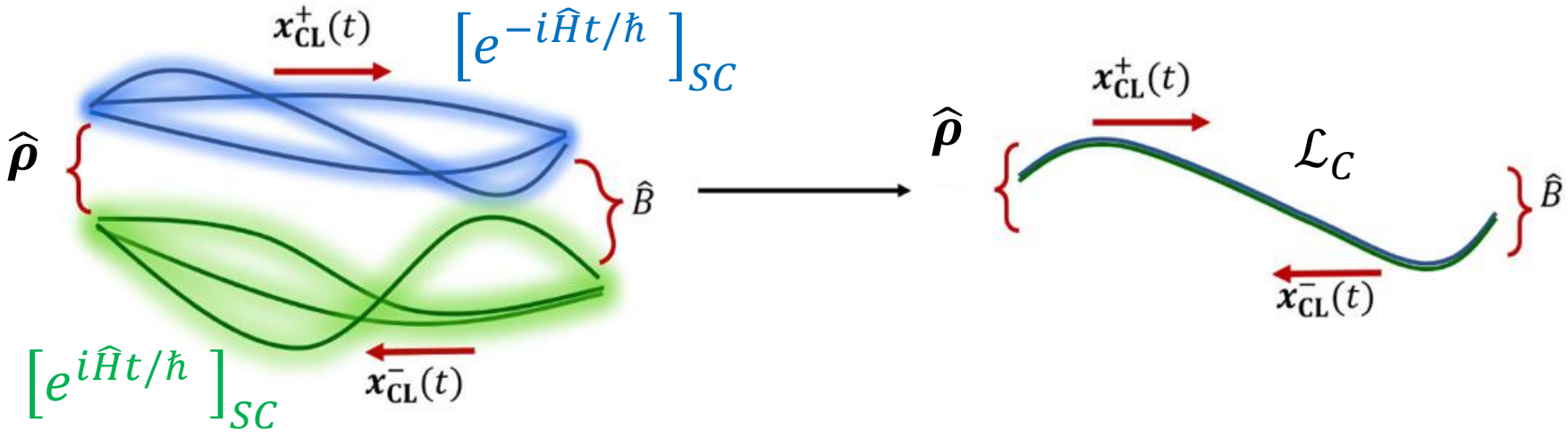
Semiclassical (SC) dynamics



- Use Stationary Phase Approximation (SPA) to path integral of propagator: Only count classical paths .
- SC pre-factor accounts for `quantum fluctuations around classical paths.
- Trajectories interfere with each other through their classical actions.
- Can account for most quantum effects: ZPE, shallow tunneling, interference.

-Miller, *J. Phys. Chem. A*, **105**, 2942 (2001)
-**Malpathak**, Church, Ananth, *J. Phys. Chem. A* **126**, 6359 (2022)

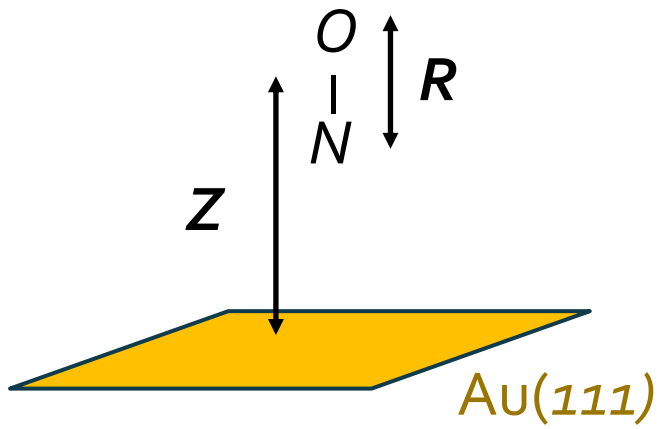
Classical-limit SC dynamics



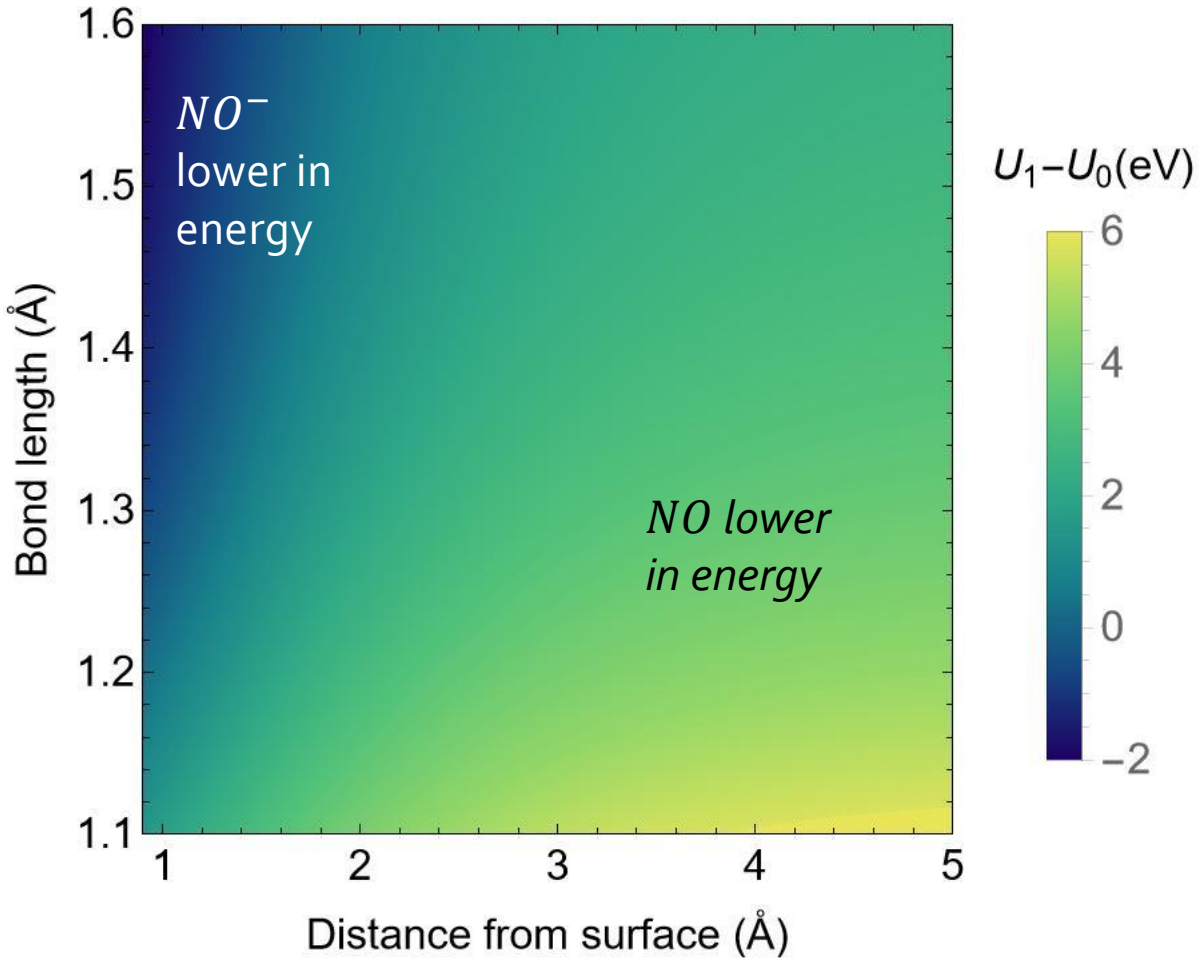
- Assume forward $[x^{+}_{Cl}(t)]$ and backward $[x^{-}_{Cl}(t)]$ trajectories coincide.
- Evolve ensemble of classical trajectories from a quantum distribution.

-Miller, *J. Phys. Chem. A*, **105**, 2942 (2001)
- Wang et. al., *J .Chem. Phys.*, 108, 9726 (1998), Sun et.al., *J .Chem. Phys.*, 109, 4190 (1998).
-**Malpathak**, Church, Ananth, *J. Phys. Chem. A* **126**, 6359 (2022)

Some insights into the scattering process



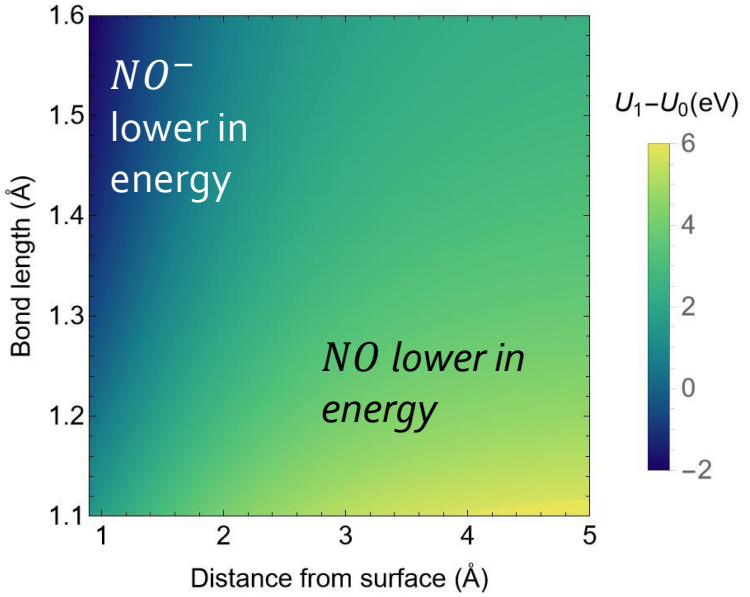
An elongated NO bond and proximity to the Au(111) surface facilitate electron transfer



- **Malpathak,** Ananth, *J. Phys. Chem. Lett.*, **15,** 794 (2024)
- Gardner, et.al. *J. Phys. Chem. C*, **127,** 15257 (2023)

Model Hamiltonian

Newns-Anderson-Holstein Hamiltonian



NO potential

NO^- potential

$$H_{NAH}(\boldsymbol{X},\boldsymbol{P}) = \frac{1}{2}\boldsymbol{P}.\boldsymbol{m}^{-1}.\boldsymbol{P} + U_0(\boldsymbol{X}) + [U_1(\boldsymbol{X}) - U_0(\boldsymbol{X})]d^\dagger d + \sum_k \epsilon_k c_k^\dagger c_k + \sum_k V_k(\boldsymbol{X})\,(d^\dagger c_k + c_k^\dagger d)$$

NO^- occupation number

Metal states

Metal-molecule coupling

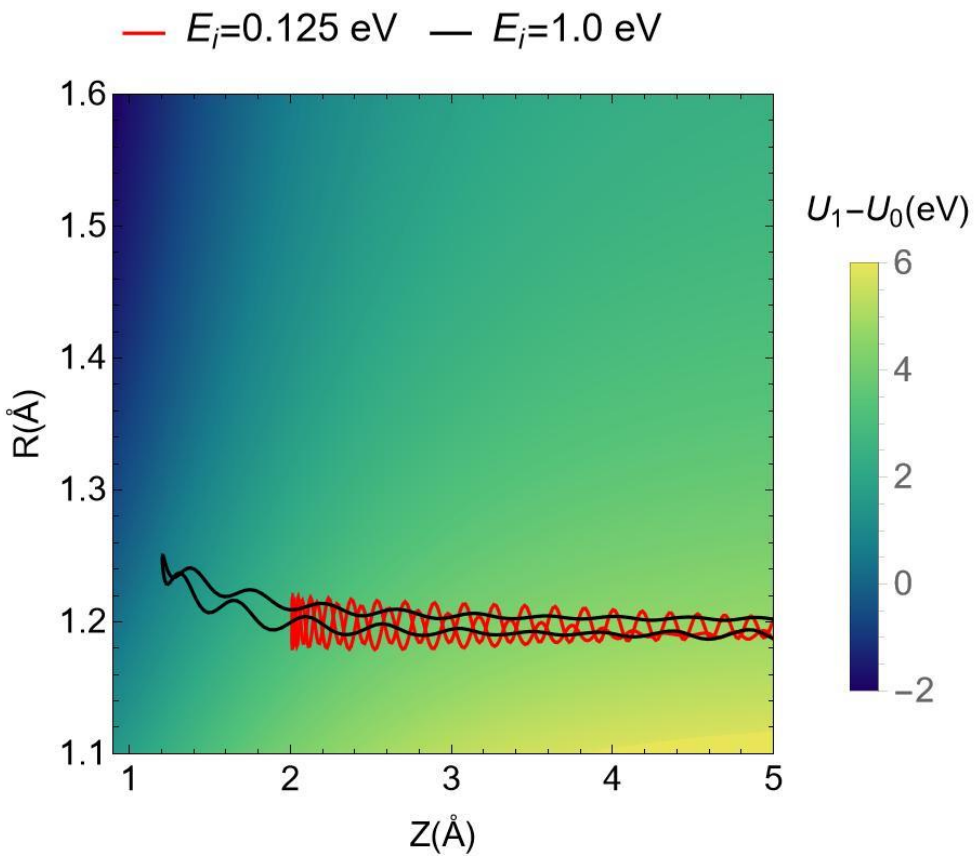
- Mapped onto continuous variables
- Use model parameters by Gardner et.al.

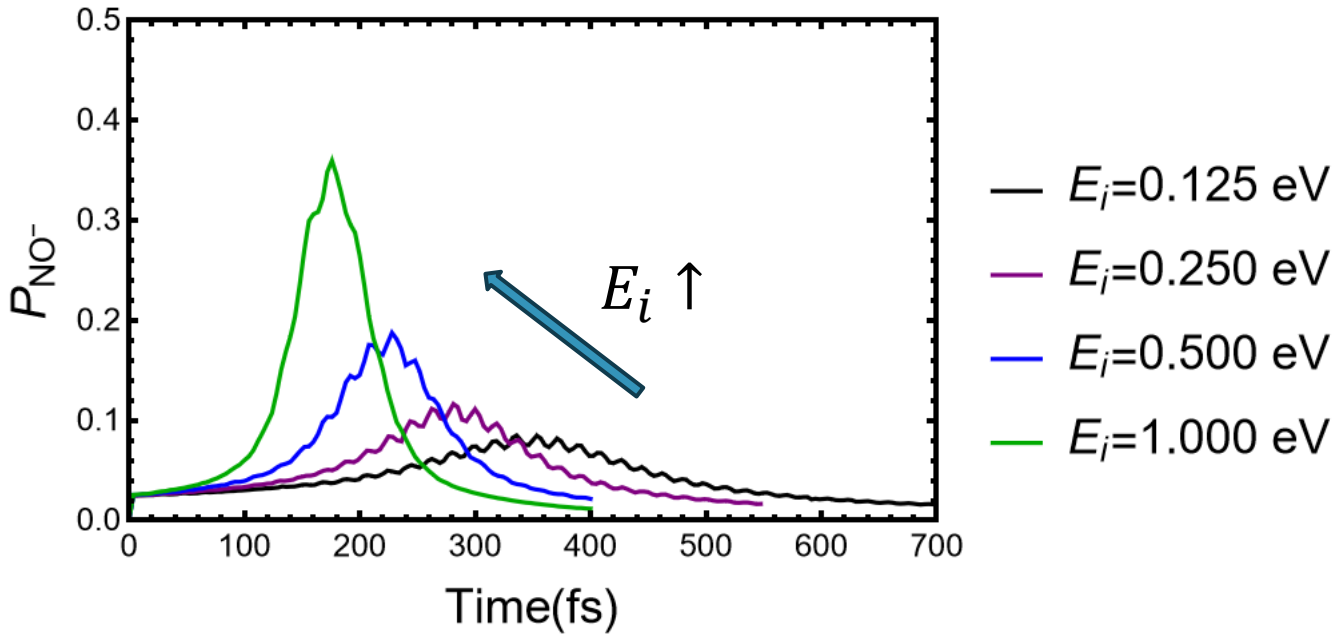
- **Malpathak,** Ananth, *J. Phys. Chem. Lett.*, **15,** 794 (2024)
- Gardner, et.al. *J. Phys. Chem. C*, **127,** 15257 (2023)

$\nu_i = 3$: shorter *NO* bond

For $\nu_i = 3$, as $E_i \uparrow$:

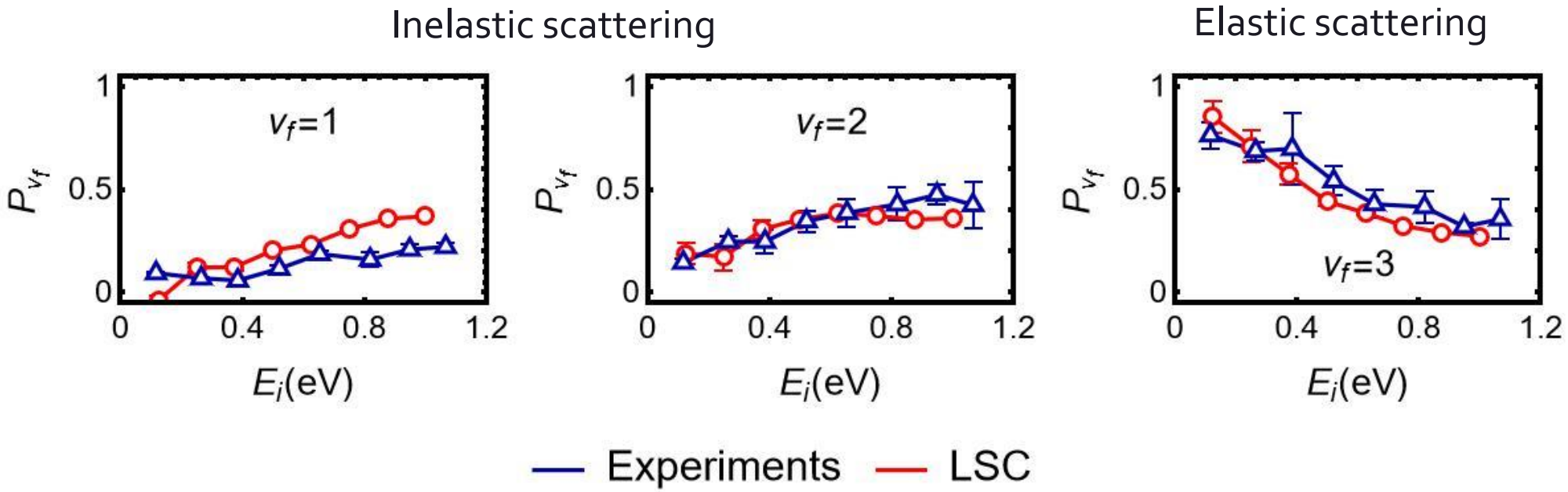
- *NO* approaches closer to surface
- Bond stretches more
- Extent of electron transfer ↑





- **Malpathak,** Ananth**,** *J. Phys. Chem. Lett.*, **15,** 794 (2024)

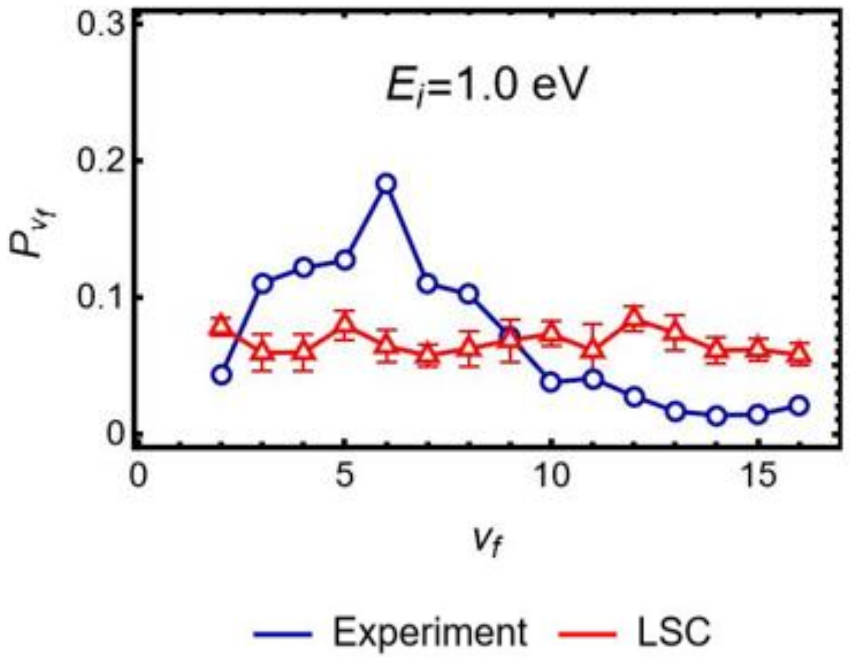
Vibrational relaxation for $v_i = 3$

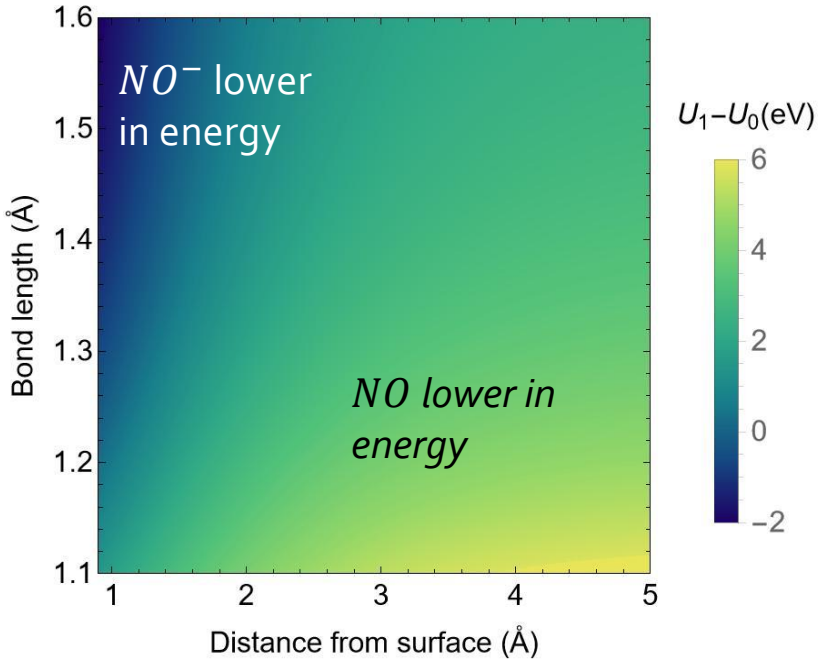


- Accurately captures role of transient electron transfer and incident translational energy
- Comparable to MDEF and IESH.

- **Malpathak,** Ananth**,** *J. Phys. Chem. Lett.*, **15,** 794 (2024)

$v_i = 16$: longer *NO* bond



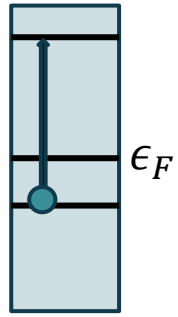


LSC is unable to predict experimental vibrational distributions.

- **Malpathak,** Ananth**,** *J. Phys. Chem. Lett.*, **15,** 794 (2024)

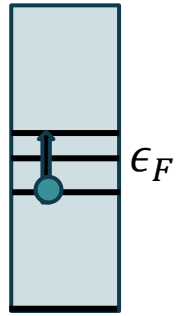
Resonant *vs.* dissipative

Vibrational energy transferred into a few *high energy* EHP excitations

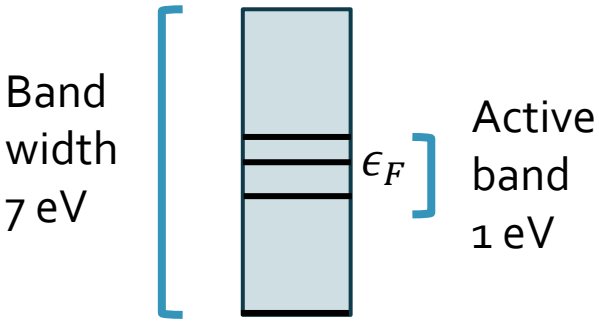


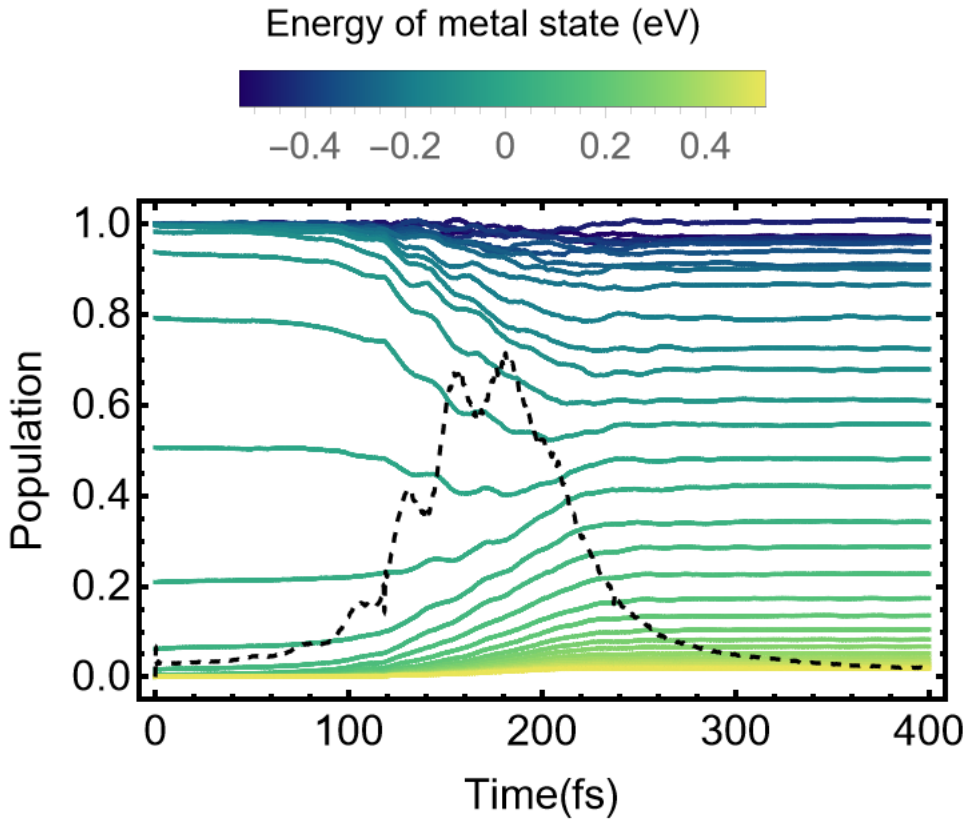
OR

Vibrational energy dissipated into many low energy EHP excitations



Population of metal states





LSC is unable to capture a resonant mechanism for electron transfer

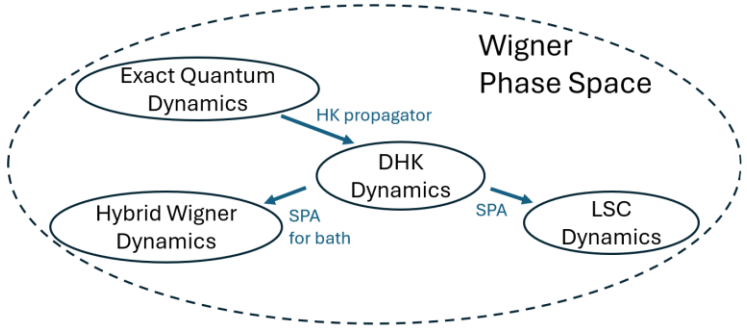
- **Malpathak,** Ananth**,** *J. Phys. Chem. Lett.*, **15,** 794 (2024)

Summary

- Can predict role of ET and dependence on translational energy in vibrational relaxation for short NO bond lengths.

- Like other state of the art methods, falls short for larger bond lengths. Unable to predict resonant ET mechanism.
- Need a better NAH model Hamiltonian that can account for orientation of NO, rotation and coupling to phonons.

- Quantizing NO vibration might provide a more accurate description of resonant ET. New method: **Hybrid Wigner Dynamics** is well suited for this.



- **Malpathak**, Ananth, *J. Phys. Chem. Lett.*, **15**, 794 (2024)
- **Malpathak**, Ananth, *in prep.*

Thank you!

Graduate Research Committee:
Prof. Nandini Ananth
Prof. Gregory Ezra
Prof. Roger Loring

Ananth Group Members

Cornell Dept. of Chemistry and
NSF for funding

Path integral for the propagator

N of these, $\epsilon = t/N$

$$\langle x'|e^{-i\hat{H}t/\hbar}\,|\,x\rangle \quad = \quad \langle x'|e^{-i\hat{H}\epsilon/\hbar}\;e^{-i\hat{H}\epsilon/\hbar}\;..e^{-i\hat{H}\epsilon/\hbar}\,|\,x\rangle$$

- $N \to \infty$
- Trotter approximation

$$= \int \mathcal{D}x \;\; e^{i\,S(x,x')/\hbar}$$

sum over paths

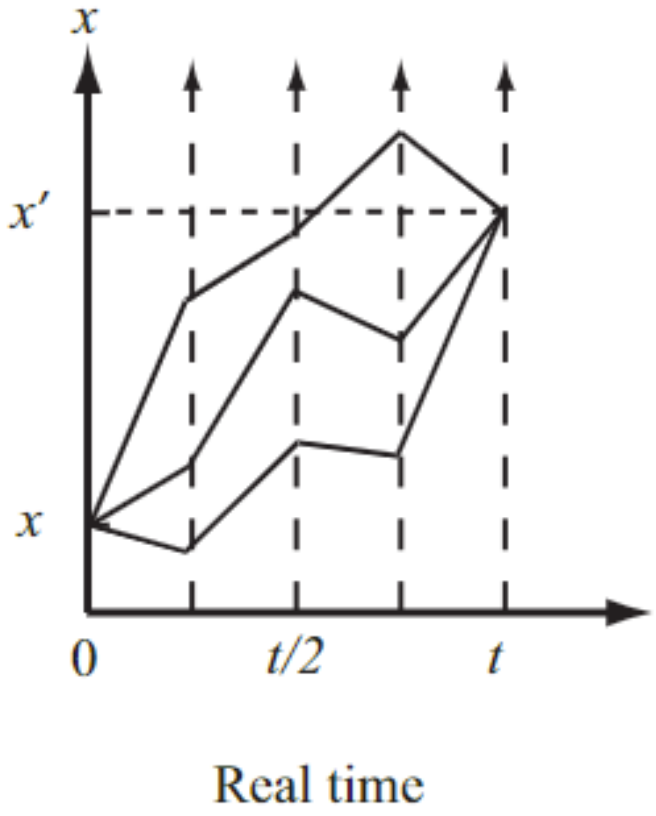
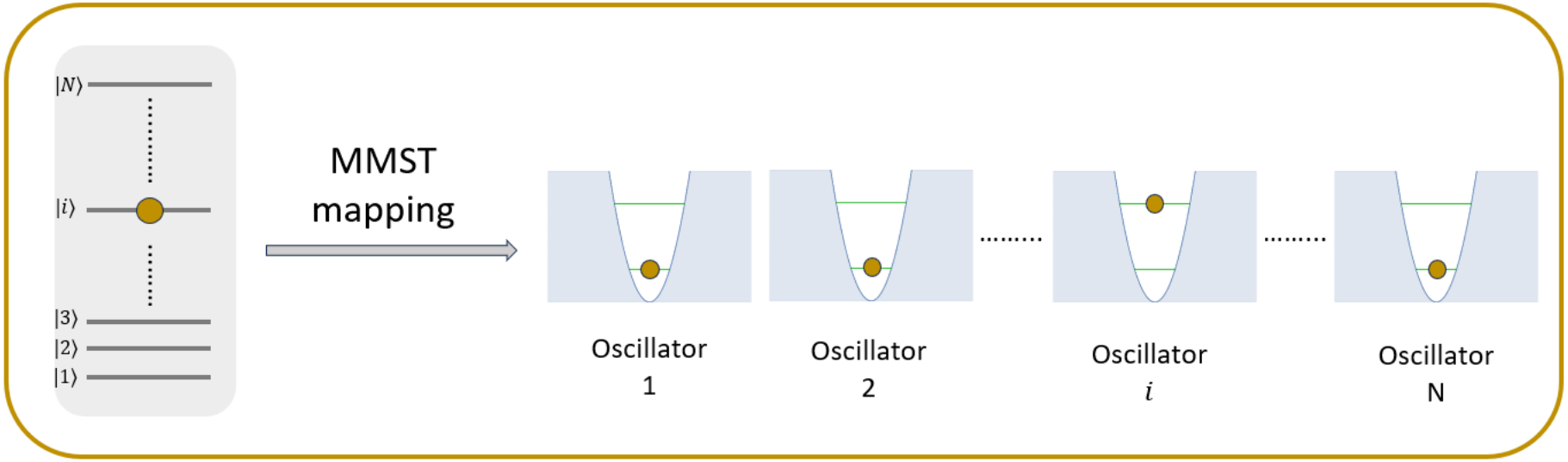


Figure from: *Stat. Mech.* by Mark Tuckerman

MMST mapping



$$H_{sym}(\mathbf{X},\mathbf{P},\mathbf{x},\mathbf{p}) = \frac{1}{2}\mathbf{P}.\mathbf{M}^{-1}.\mathbf{P} + \tilde{U}(\mathbf{X}) + \frac{1}{2}\left[\mathbf{x}.\tilde{\mathbf{V}}(\mathbf{X}).\mathbf{x} + \mathbf{p}.\tilde{\mathbf{V}}(\mathbf{X}).\mathbf{p}\right],$$

$$\tilde{U}(\mathbf{X}) = U_0(\mathbf{X}) + \frac{N_e}{N+1}\mathrm{Tr}[V(\mathbf{X})] \qquad \tilde{\mathbf{V}}(\mathbf{X}) = \mathbf{V}(\mathbf{X}) - \frac{1}{N+1}\mathrm{Tr}[V(\mathbf{X})]\mathbb{1}$$

Initial Sampling

$$\hat{\rho} = |P_{Zi}, Z_i\rangle\langle P_{Zi}, Z_i| \otimes |\nu_i\rangle\langle\nu_i| \otimes \hat{\rho}_{\mathrm{mol}} \otimes \hat{\rho}_{\mathrm{metal}}.$$

Electronic dofs sampled using focused sampling. $\frac{1}{2}(x_k^2 + p_k^2 - \gamma) = n_k.$

In spin mapping $\gamma \to 0 \; as \; N \to \infty$

-Bonella &Coker, Journal of Chemical Physics 2003, 118, 4370–4385
-Runeson & Richardson, The Journal of Chemical Physics 2019, 151, 044119.

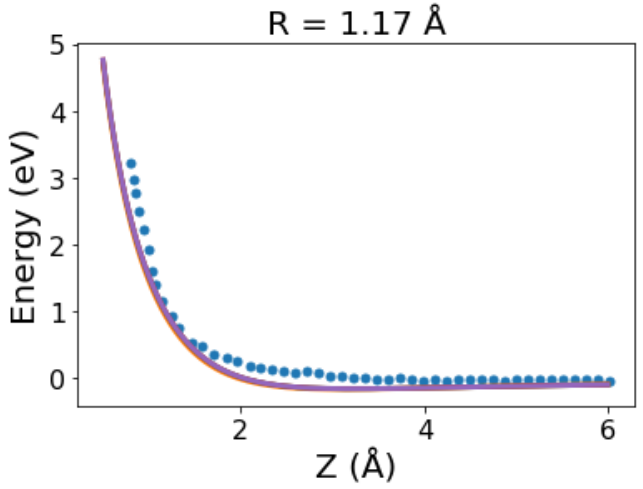
Replacing fermionic operators with bosonic ones

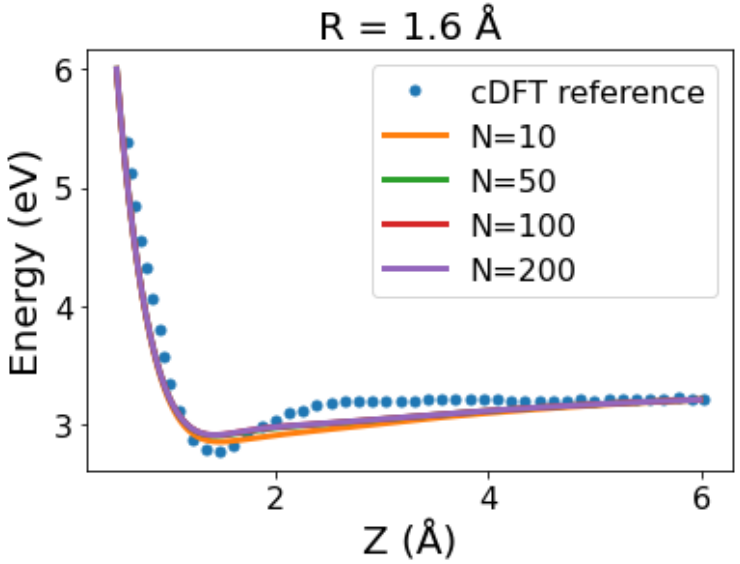
$$\langle \mathbf{n}|\hat{c}_j^\dagger(t_1)\hat{c}_k(t_2)|\mathbf{n}\rangle = \sum_{j',k'} G^*_{j',j}(t_1)G_{k,k'}(t_2)\delta_{j',k'}\delta_{n'_k,1}$$
$$= \langle \mathbf{n}|\hat{b}_j^\dagger(t_1)\hat{b}_k(t_2)|\mathbf{n}\rangle, \qquad (20a)$$

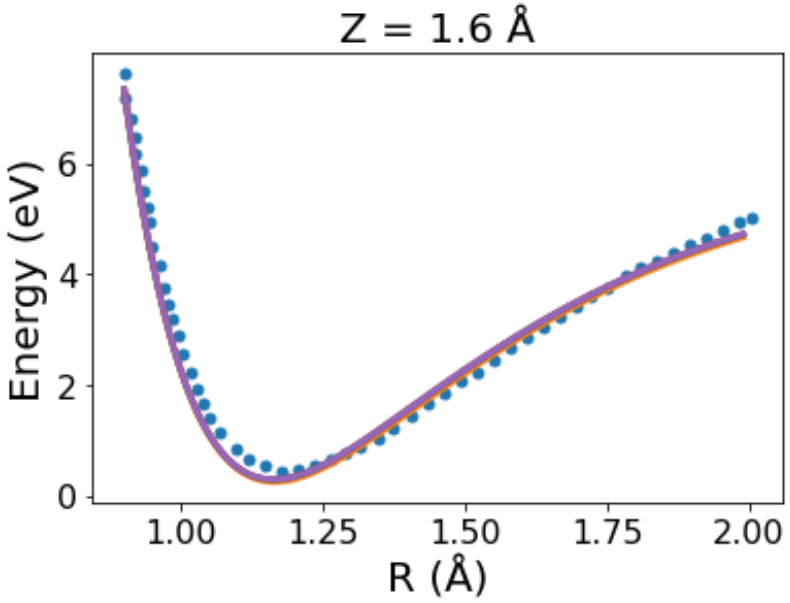
$$\langle \mathbf{n}|\hat{c}_k(t_2)\hat{c}_j^\dagger(t_1)|\mathbf{n}\rangle = \sum_{j',k'} G^*_{j',j}(t_1)G_{k,k'}(t_2)\delta_{j',k'}\delta_{n'_k,0}$$
$$= \langle \mathbf{n}|\hat{b}_k(t_2)\hat{b}_j^\dagger(t_1)|\mathbf{n}\rangle. \qquad (20b)$$

-J. *Chem. Phys.***158,** 094112 (2023);

GHM Refit


R = 1.17 Å
Energy (eV)
Z (Å)
0
1
2
3
4
5
2
4
6


R = 1.6 Å
Energy (eV)
Z (Å)
cDFT reference
N=10
N=50
N=100
N=200
3
4
5
6
2
4
6


Z = 1.6 Å
Energy (eV)
R (Å)
0
2
4
6
1.00
1.25
1.50
1.75
2.00

GHM Refit

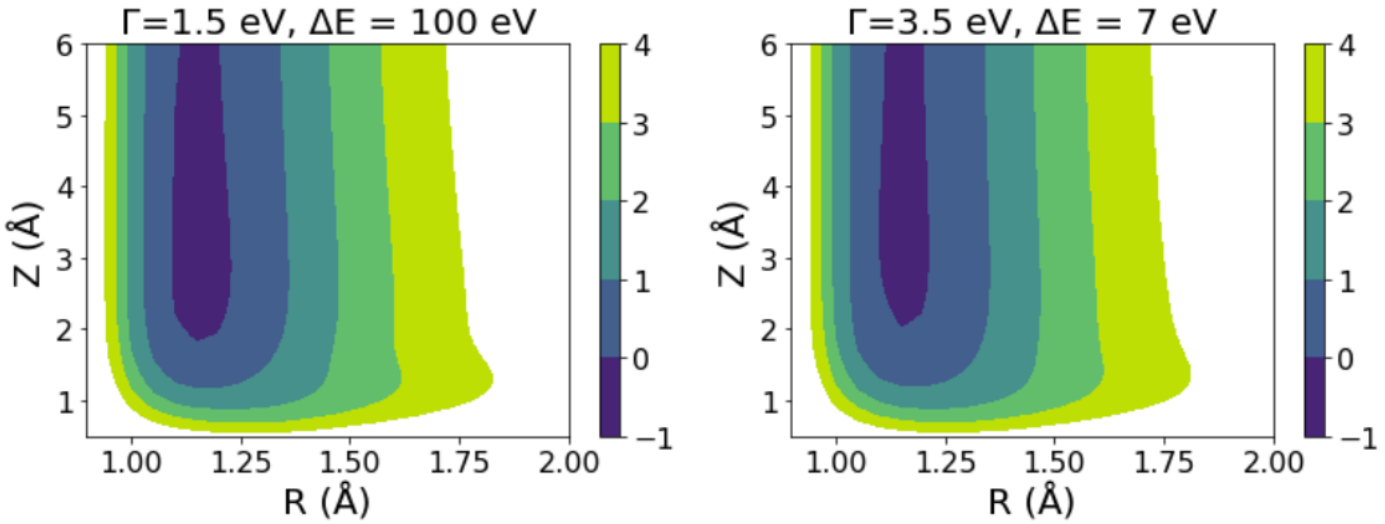
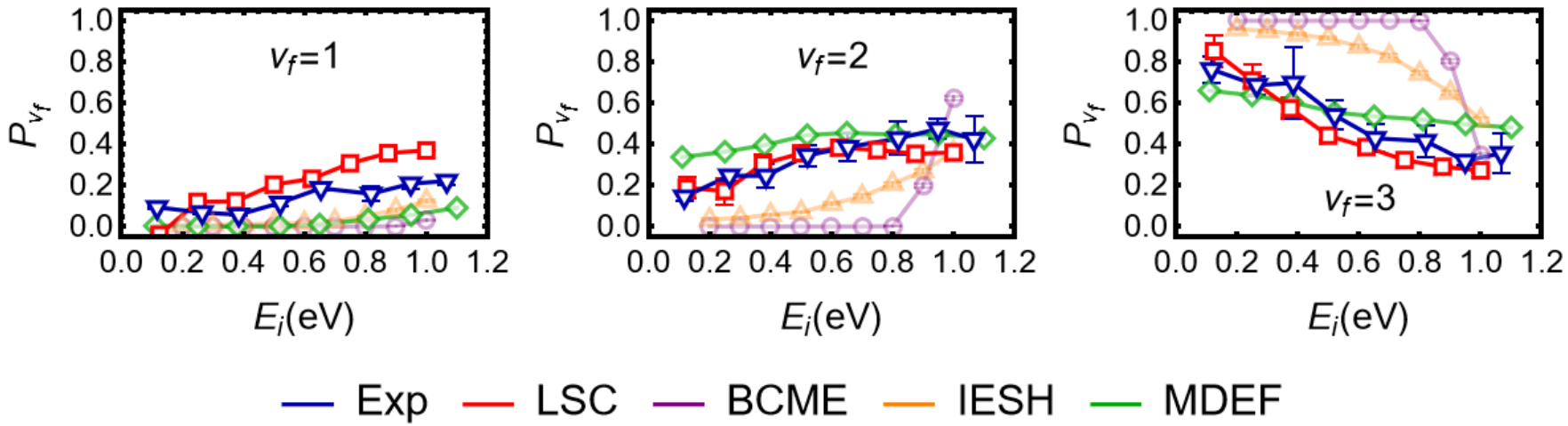
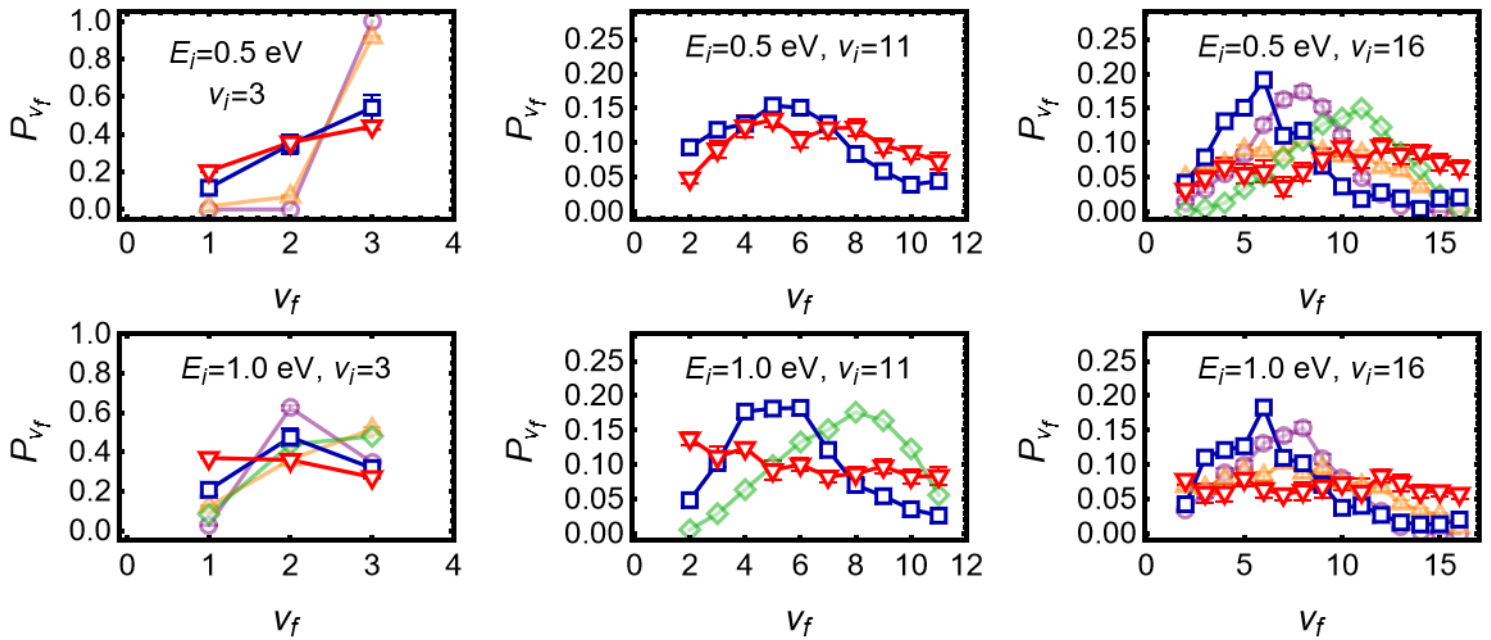


Figure S3: Contour plots of the adiabatic ground state energy for the model of Gardner et al. ($\Gamma = 1.5\text{eV}, \Delta E = 100\text{eV}$) and our refit potential ($\Gamma = 3.5\text{eV}, \Delta E = 7\text{eV}$).


v_f=1
v_f=2
v_f=3
P_{v_f}
E_i(eV)
Exp
LSC
BCME
IESH
MDEF


E_i=0.5 eV
v_i=3
E_i=0.5 eV, v_i=11
E_i=0.5 eV, v_i=16
E_i=1.0 eV, v_i=3
E_i=1.0 eV, v_i=11
E_i=1.0 eV, v_i=16
P_{v_f}
v_f
Exp.
LSC
BCME
IESH
MDEF