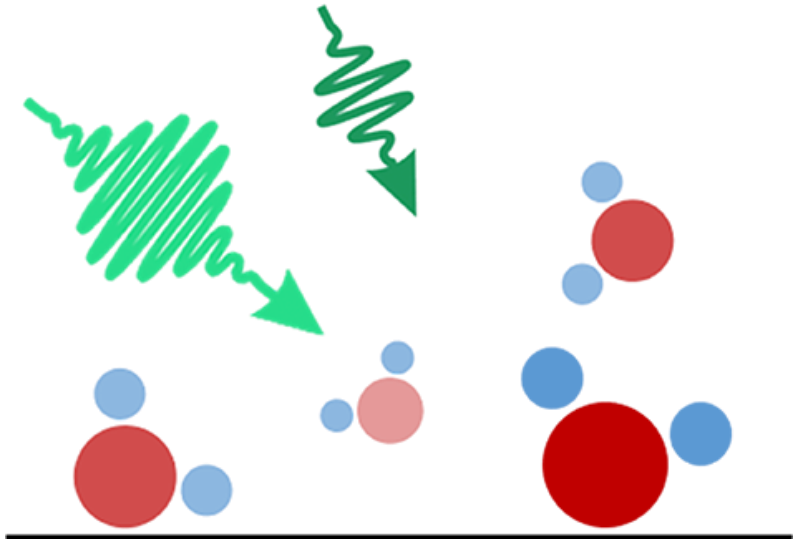
USC University of Southern California

How to calculate NAC with PW accurately and efficiently



VISTA

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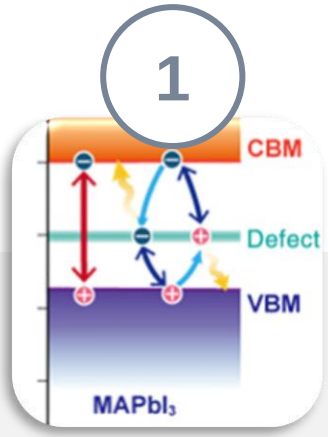
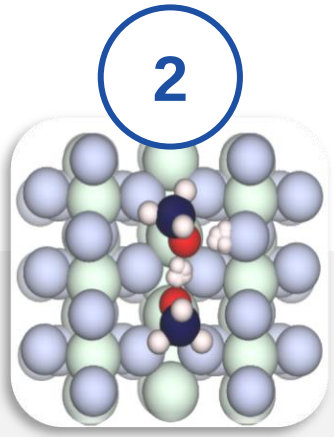
1) Why an accurate NAC is important



Non-radiative Recombination

Error accumulation



Non-adiabatic Ring polymer molecular dynamics

Bead average NAC

Machine Learning

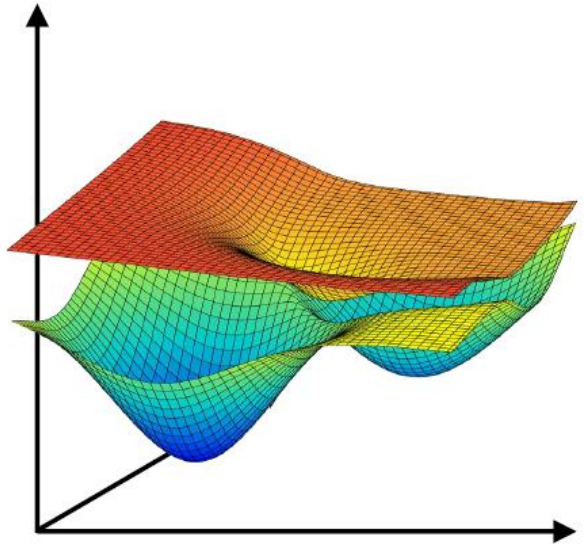
Predictive NAC

2) What is NAC

$$i\hbar \frac{\partial \Psi(\boldsymbol{r}, \boldsymbol{R}, t)}{\partial \mathrm{t}} = H(\boldsymbol{r}, \boldsymbol{R}, t)\Psi(\boldsymbol{r}, \boldsymbol{R}, t)$$

$$\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \sum_j c_j(t)\psi_j\big(\boldsymbol{r}; \boldsymbol{R}(t)\big)$$

$$i\hbar \frac{\partial c_j(t)}{\partial \mathrm{t}} = \sum_k c_k(t)\big[\varepsilon_j \delta_{jk} - i\hbar \boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}}\big]$$



Non-adiabatic coupling (scalar)

$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \langle \psi_j | \nabla_{\boldsymbol{R}} | \psi_k \rangle \cdot \dot{\boldsymbol{R}} = \frac{\left\langle \psi_j \middle| \nabla_{\boldsymbol{R}} \hat{H} \middle| \psi_k \right\rangle}{\varepsilon_k - \varepsilon_j} \cdot \dot{\boldsymbol{R}}$$

HST Equation

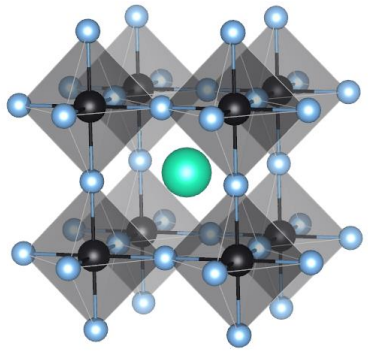
$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \psi_j \middle| \frac{\partial}{\partial t} \middle| \psi_k \right\rangle = \frac{1}{2dt}\big(\langle \psi_j(r,t) | \psi_k(r, t+dt) \rangle - \langle \psi_j(r, t+dt) | \psi_k(r,t) \rangle\big)$$

ψ_j Adiabatic Wavefunction

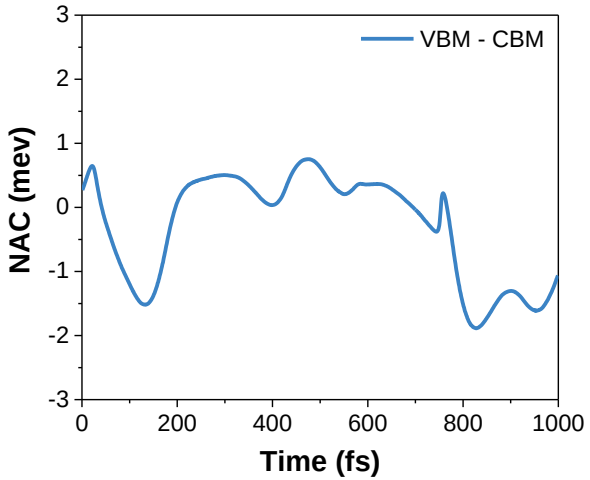
- **Planewaves Basis Set**
- Atomic Basis Set
- Mixed

Widely used in
Condensed matter systems
Metal; Surface; Solid

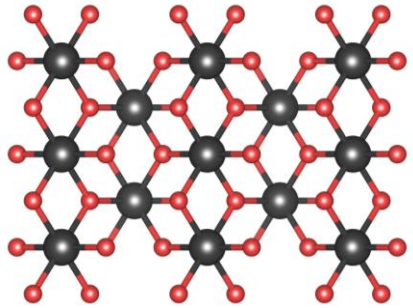
3) What are NACs look like



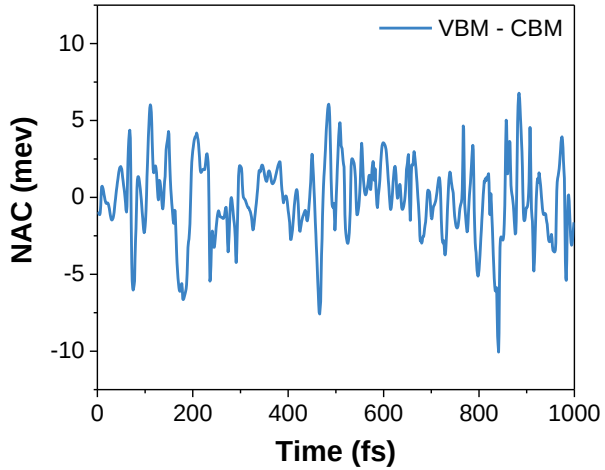
Halide Perovskite



Interband relaxation only couples
with ultra low-frequency lattice phonon

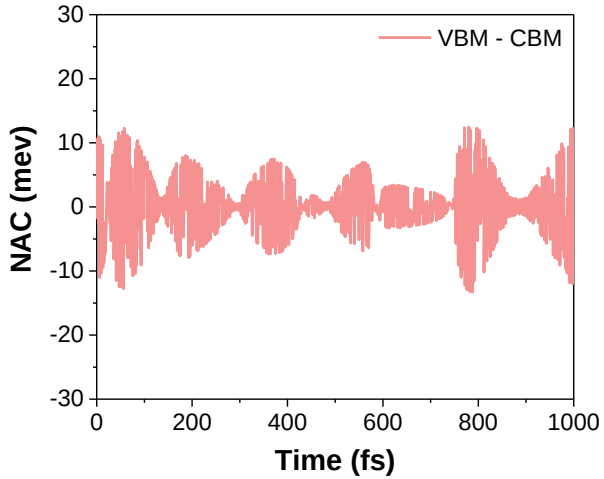


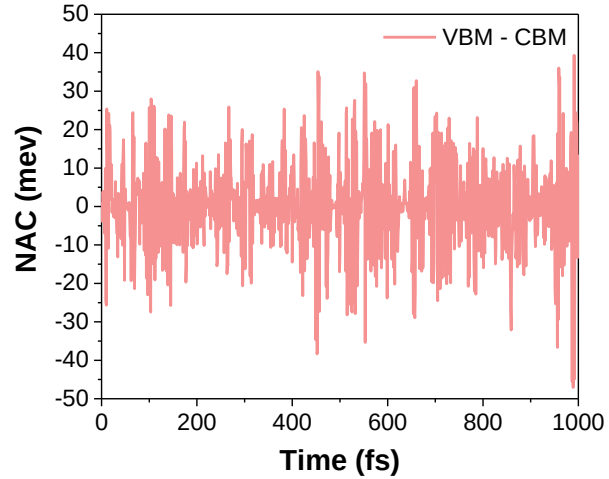
TiO_2



Calculated with CAnac (All corrections are included)

Before





Conventional NAC without any correction

Basic concepts about PAW

- **Frozen core approximation**

No core orbitals are taken into account in the whole calcualtion

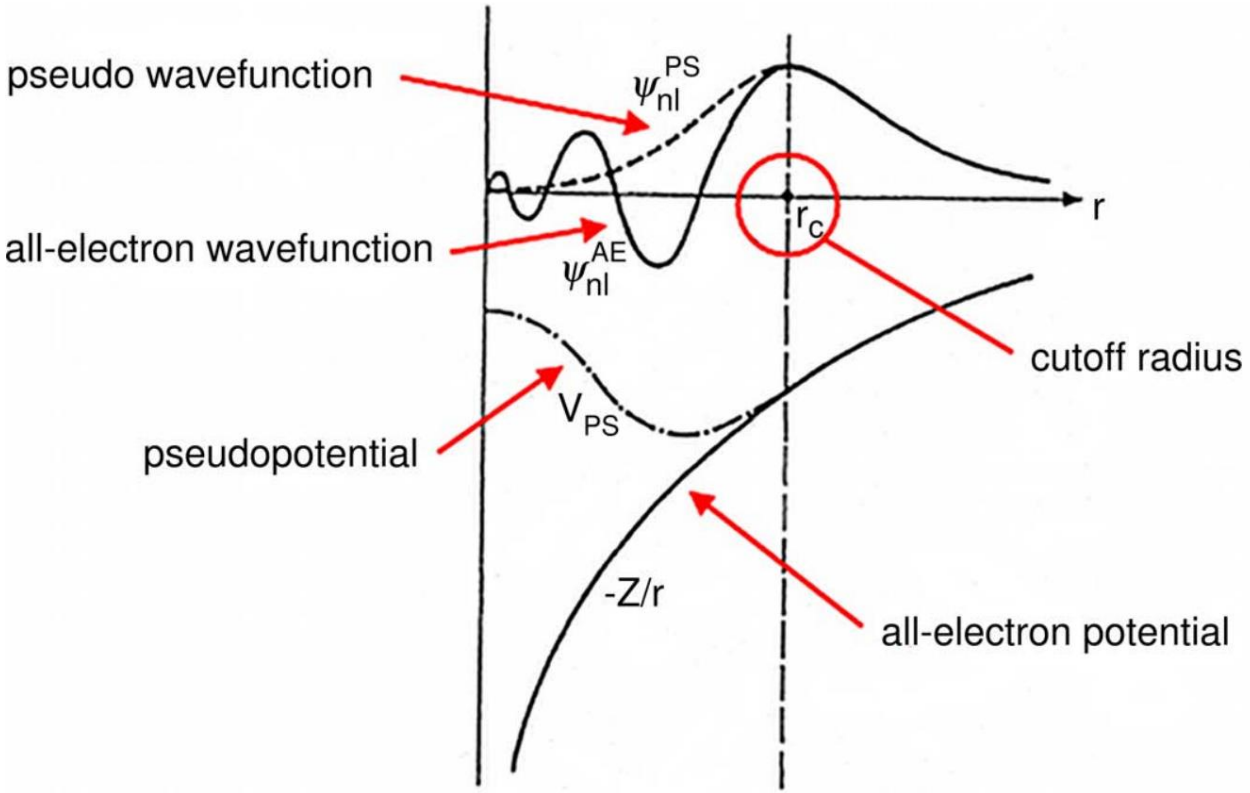
- **The all-electron (AE) wavefunction in PAW, also known as true or exact wavefunction, has nothing to do with the core electrons wavefunction (e.g. WIN2K)**

- AE wavefunction oscillates sharply within the core region

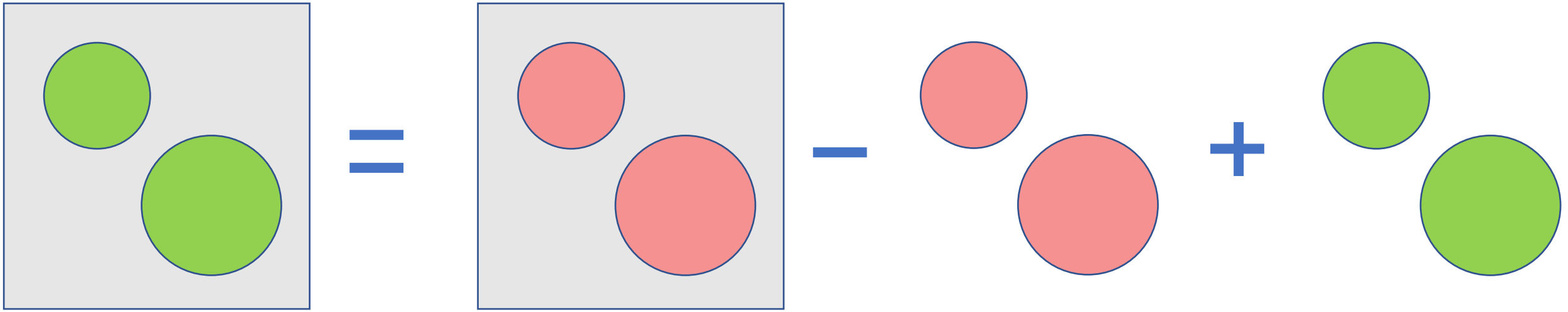
Large cutoff; Expensive

- PS wavefunction is identical with corresponding AE wavefunction outside the core region

Small cutoff; Efficient; **But wrong shape in the core region**



Basic concepts about PAW



AE = PS − PS-onsite + AE-onsite

$$|\psi_k\rangle = \hat{\mathcal{T}}|\tilde{\psi}_k\rangle = |\tilde{\psi}_k\rangle + \sum_a \sum_i \left(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle\right)\langle \tilde{p}_i^a | \tilde{\psi}_k\rangle$$

ψ_k All electron Wavefunction $\tilde{\psi}_k$ Pseudo Wavefunction

ϕ_i^a i^{th} AE partial wave of atom a $\tilde{\phi}_i^a$ i^{th} AE partial wave of atom a $\tilde{p}_i^a$ Projector function

Exact NAC with PAW

$$|\psi_k\rangle = \hat{\mathcal{T}}|\tilde{\psi}_k\rangle = |\tilde{\psi}_k\rangle + \sum_a \sum_i \left(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle\right)\langle \tilde{p}_i^a|\tilde{\psi}_k\rangle$$

HST Equation

$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \psi_j \middle| \frac{\partial}{\partial t} \middle| \psi_k \right\rangle = \frac{1}{2dt}\left(\langle \psi_j(r,t)|\psi_k(r,t+dt)\rangle - \langle \psi_j(r,t+dt)|\psi_k(r,t)\rangle\right)$$

- AE WFN has never been used in the SCF calculation
- PS WFN is based on PW grids, while other partial waves and projector function are based on atom centered radial grids.
- PS WFN is readily available (VASP WAVECAR QE pwscf.save/K0001 etc.)

- **So people used PS WFNs instead without rigid test for a long time**

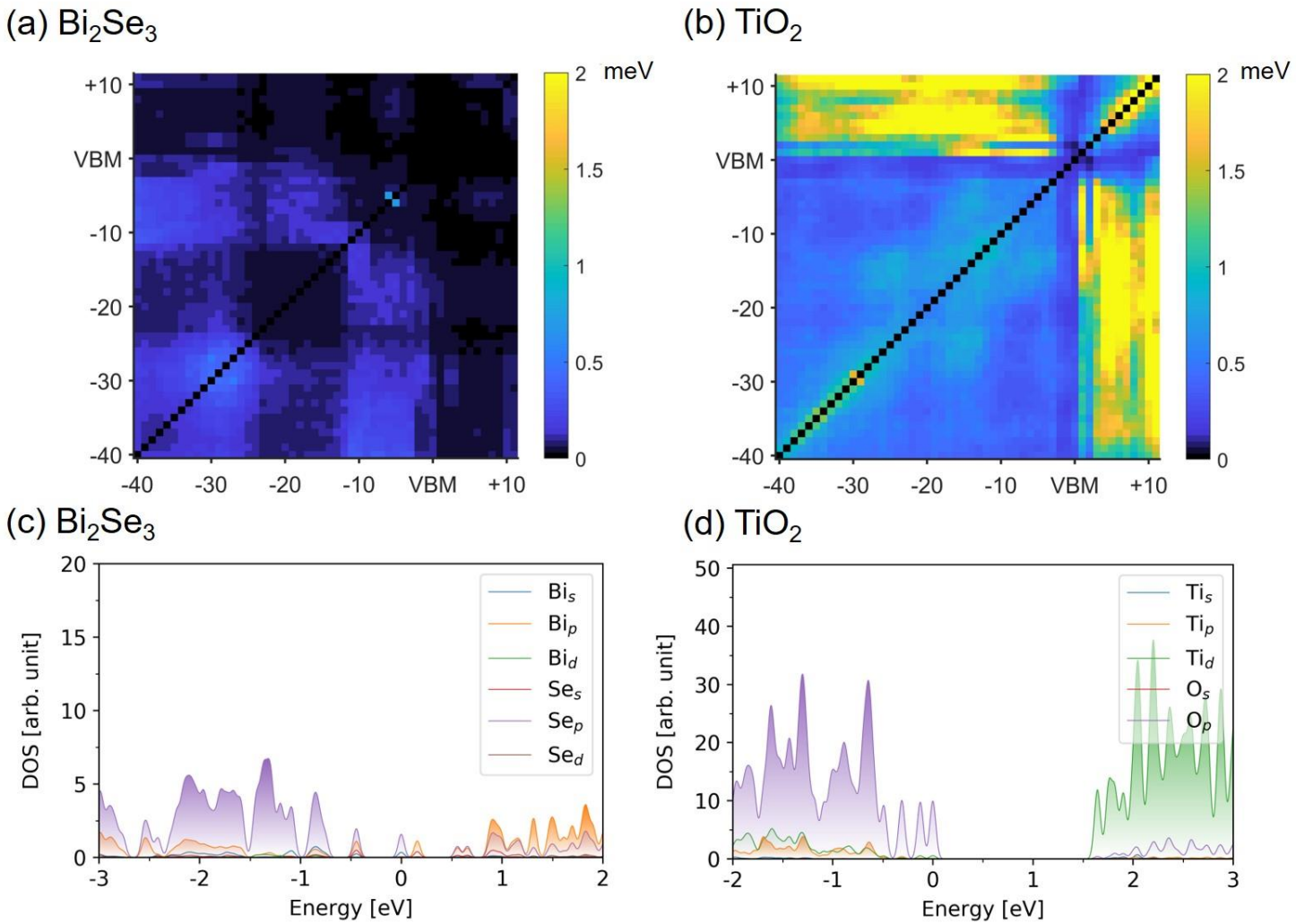
$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \tilde{\psi}_j \middle| \frac{\partial}{\partial t} \middle| \tilde{\psi}_k \right\rangle = \frac{1}{2dt}\left(\langle \tilde{\psi}_j(r,t)|\tilde{\psi}_k(r,t+dt)\rangle - \langle \tilde{\psi}_j(r,t+dt)|\tilde{\psi}_k(r,t)\rangle\right)$$

- **PS WFNs are neither orthonormal nor eigen wavefunction**

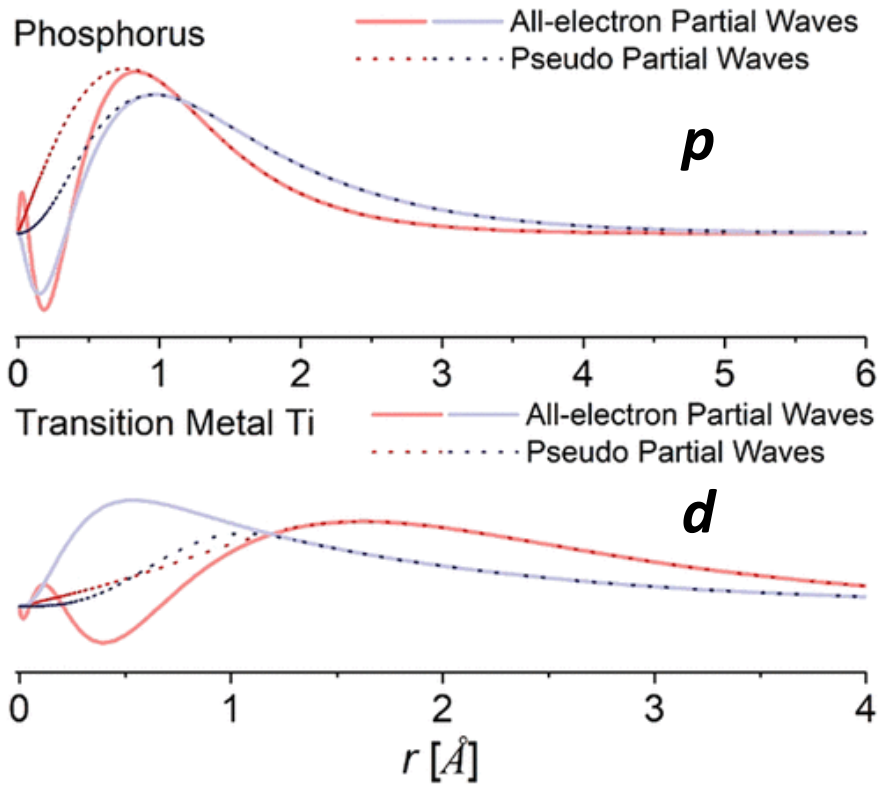
PS NAC fails for transition metal

$$|\psi_k\rangle = \hat{\mathcal{T}}|\tilde{\psi}_k\rangle = |\tilde{\psi}_k\rangle + \sum_a \sum_i (|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle)\langle \tilde{p}_i^a|\tilde{\psi}_k\rangle$$

Deviation between exact NAC and PS NAC



ϕ_i^a $\tilde{\phi}_i^a$



JPCL **2020** 11, 10073-10080

Exact NAC with PAW

$$|\psi_k\rangle = \hat{\mathcal{T}}|\tilde{\psi}_k\rangle = |\tilde{\psi}_k\rangle + \sum_a \sum_i \left(|\phi_i^a\rangle - |\tilde{\phi}_i^a\rangle\right)\langle \tilde{p}_i^a|\tilde{\psi}_k\rangle$$

$$\chi_k^a = \sum_i |\phi_i^a(r)\rangle\langle \tilde{p}_i^a|\tilde{\psi}_k\rangle \qquad \tilde{\chi}_k^a = \sum_i |\tilde{\phi}_i^a(r)\rangle\langle \tilde{p}_i^a|\tilde{\psi}_k\rangle$$

For any operator A

$$\langle\psi_j|A|\psi_k\rangle = \langle\tilde{\psi}_j + \textstyle\sum_a (\chi_j^a - \tilde{\chi}_j^a)\,|A|\tilde{\psi}_k + \sum_a (\chi_k^a - \tilde{\chi}_k^a)\rangle$$

$$= \langle\tilde{\psi}_j|A|\tilde{\psi}_k\rangle + \sum_a \left(\langle\chi_j^a|A|\chi_k^a\rangle - \langle\tilde{\chi}_j^a|A|\tilde{\chi}_k^a\rangle\right) + \quad (1)$$

$$\textstyle\sum_a \langle(\chi_j^a - \tilde{\chi}_j^a)|A|\tilde{\psi}_k - \tilde{\chi}_k^a\rangle + \sum_a \langle\tilde{\psi}_j - \tilde{\chi}_j^a|A|(\chi_k^a - \tilde{\chi}_k^a)\rangle + \quad (2)$$

$$\textstyle\sum_a \sum_{a',a'\neq a}\langle(\chi_j^a - \tilde{\chi}_j^a)|A|(\chi_k^{a'} - \tilde{\chi}_k^{a'})\rangle \quad (3)$$

$$\langle\tilde{p}_i^a|\tilde{\phi}_j^a\rangle = \delta_{ij} \qquad \phi_i^a(r) = \tilde{\phi}_i^a(r) \quad |r - R_0| > r_c \qquad \tilde{\psi}_k(r) = \sum_i |\tilde{\phi}_i^a(r)\rangle\langle\tilde{p}_i^a|\tilde{\psi}_k\rangle \quad |r - R_0| < r_c$$

If A is a local operator, Term 2 and Term 3 are zero

However d/dt is a nonlocal operator

Concentric Approximation (CA) NAC

- **Main idea :**

If you don't know how to calculate it, consider to neglect it

PW x PW; PW x Radial; Radial x Radial (different center)

PW x PW; Radial x Radial (concentric)

- **But this is science :**

Prove approximation is reasonable

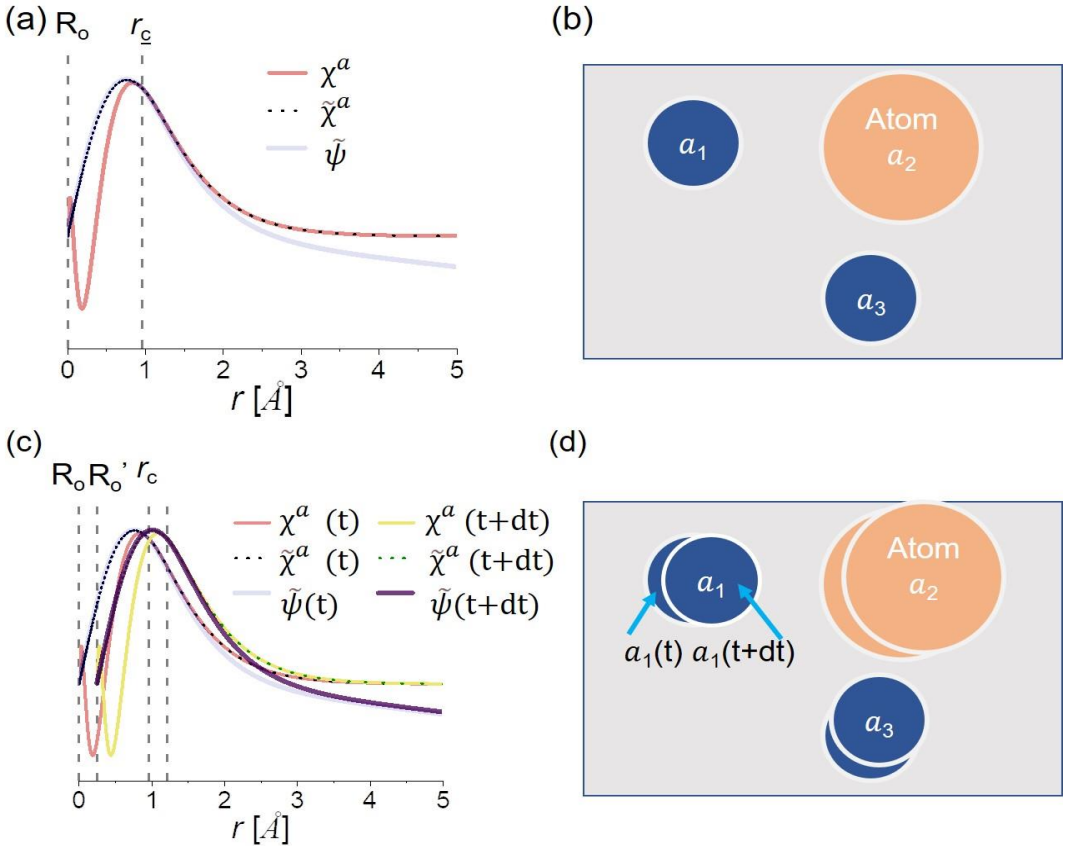
Atom center moves much slower ~<0.2% of core radius in 1 fs

$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \psi_j \middle| \frac{\partial}{\partial t} \middle| \psi_k \right\rangle$$

$$= \frac{1}{2dt}\left(\left\langle \tilde{\psi}_j(r,t) \middle| \tilde{\psi}_k(r,t+dt) \right\rangle - \left\langle \tilde{\psi}_j(r,t+dt) \middle| \tilde{\psi}_k(r,t) \right\rangle\right)$$

$$+ \frac{1}{2dt} \sum_a \sum_i \sum_{i'} C^{*a}_{j,i}(t)\left(\left\langle \phi^a_i \middle| \phi^a_{i'} \right\rangle - \left\langle \tilde{\phi}^a_i \middle| \tilde{\phi}^a_{i'} \right\rangle\right) C^{\ a}_{k,i'}(t+dt)$$

$$- \frac{1}{2dt} \sum_a \sum_i \sum_{i'} C^{*a}_{j,i}(t+dt)\left(\left\langle \phi^a_i \middle| \phi^a_{i'} \right\rangle - \left\langle \tilde{\phi}^a_i \middle| \tilde{\phi}^a_{i'} \right\rangle\right) C^{\ a}_{k,i'}(t)$$

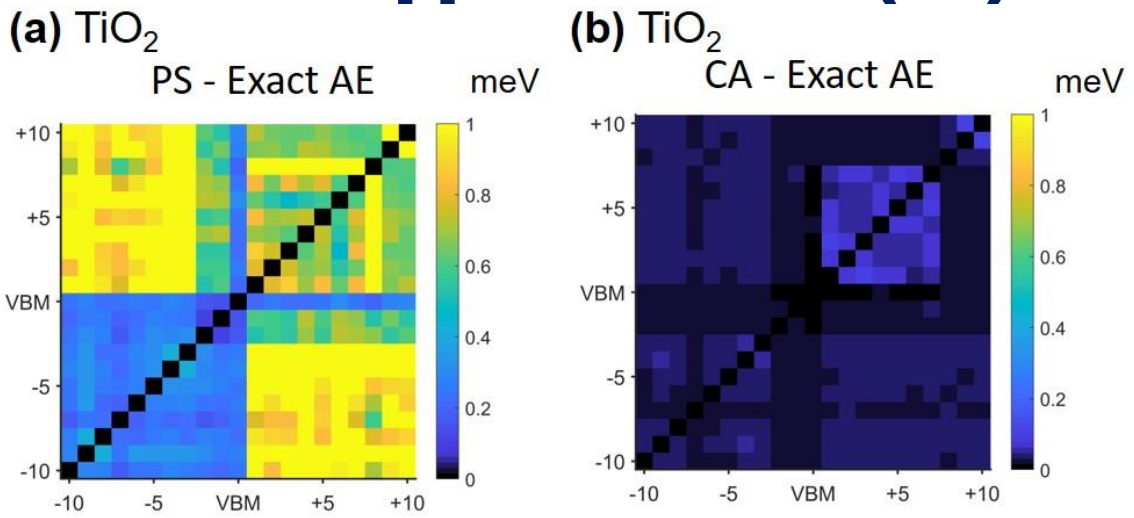


$\left\langle \phi^a_i \middle| \phi^a_{i'} \right\rangle - \left\langle \tilde{\phi}^a_i \middle| \tilde{\phi}^a_{i'} \right\rangle$ **constant for given pseudopotential**

$C^{\ a}_{k,i'}$ **readily available for every SCF employ PAW**

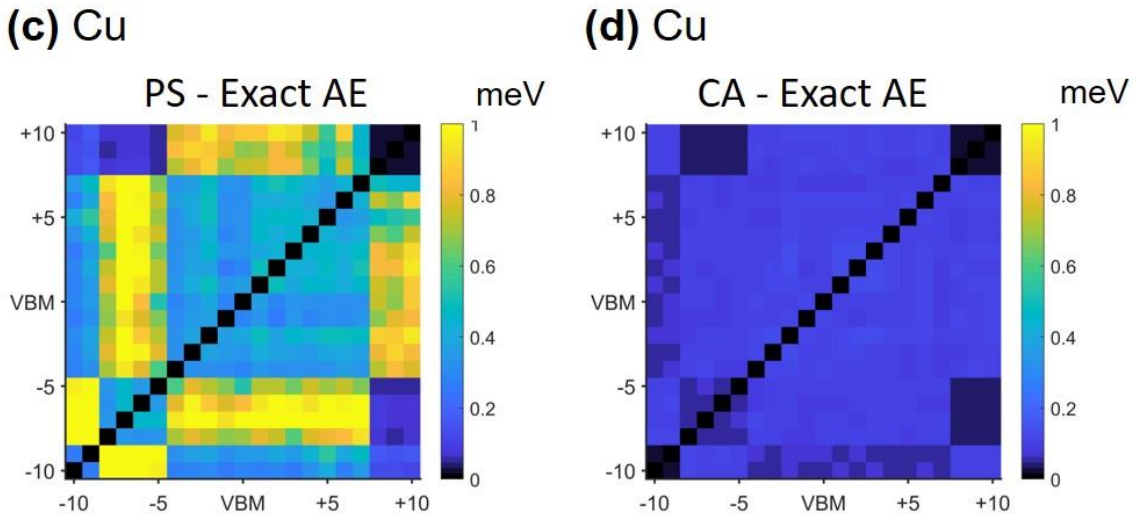
JPCL **2021** 12, 3082-3089

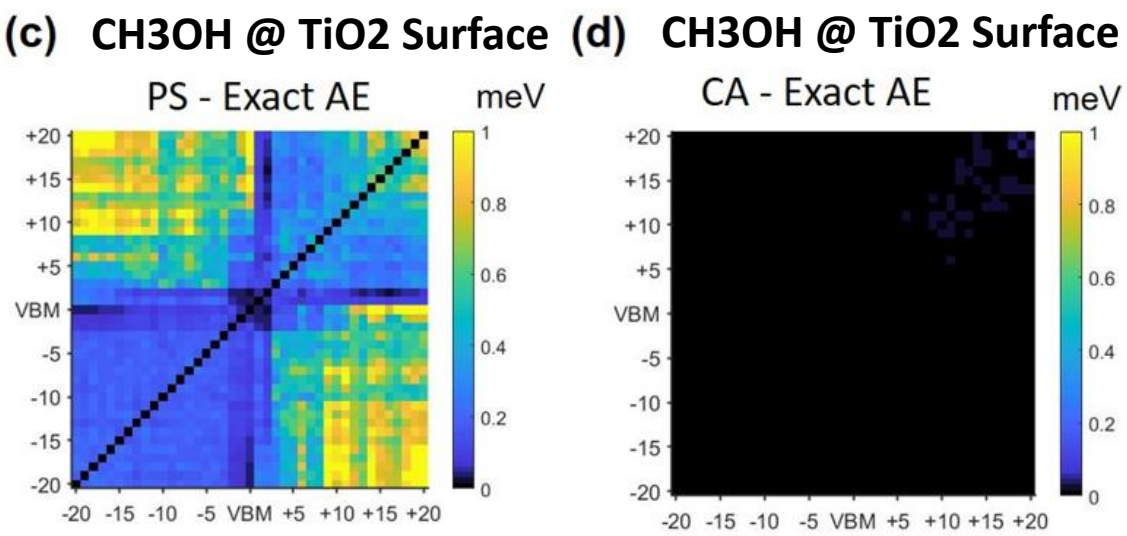
Concentric Approximation (CA) NAC



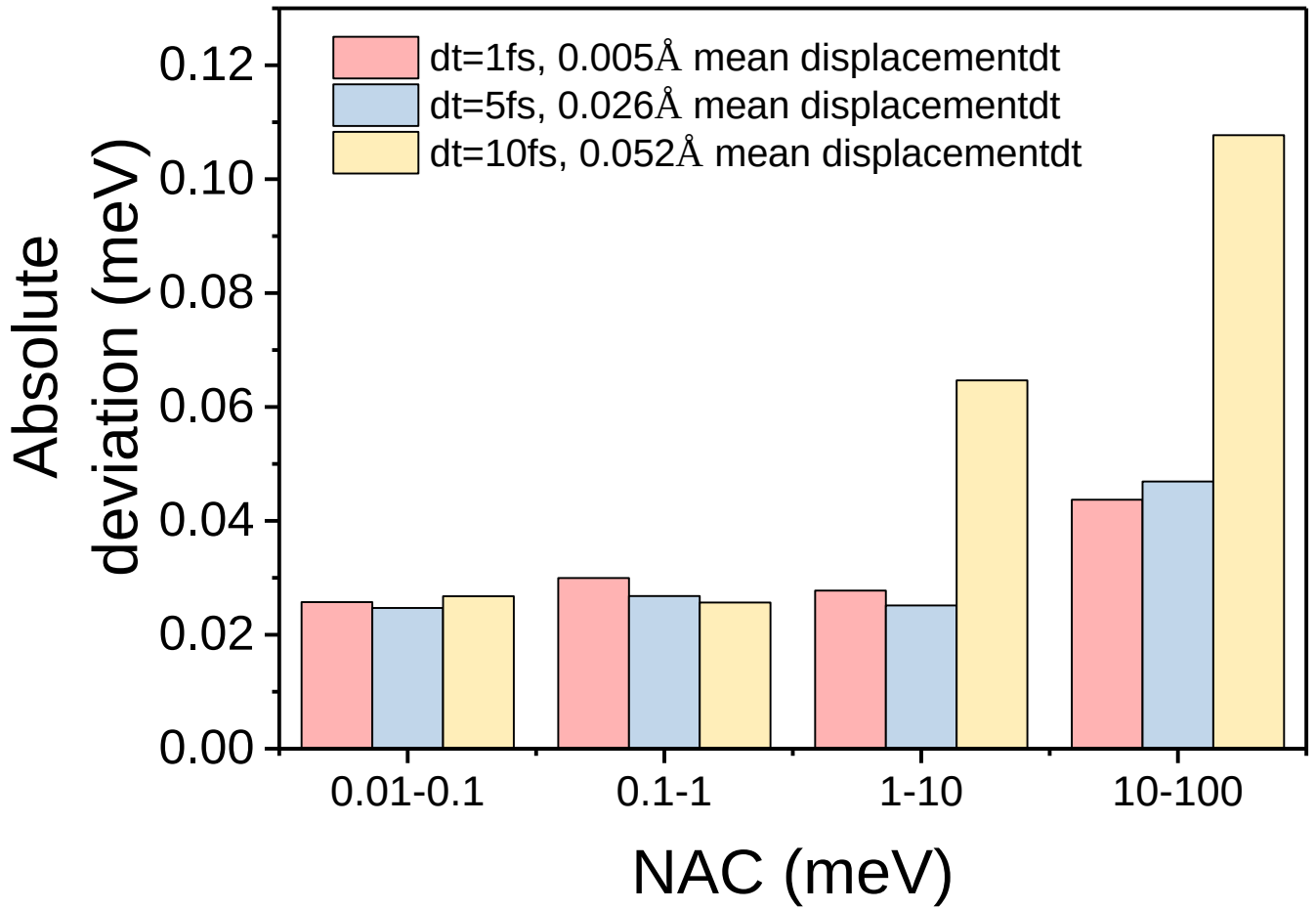
	Exact NAC	CA NAC
Calculation Time	**3~8 minutes**	**0.03 s + IO 0.5 s**

Even exact NAC code needs to consider some approximation





Concentric Approximation (CA) NAC



dt ~ 10fs, which is too large to be used in practical NAMD simulations

CA method still proved reliable

Revisit HST Equation

HST Equation

$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \psi_j \middle| \frac{\partial}{\partial t} \middle| \psi_k \right\rangle = \frac{1}{2dt}\left(\langle \psi_j(r,t) | \psi_k(r,t+dt)\rangle - \langle \psi_j(r,t+dt) | \psi_k(r,t)\rangle\right)$$

Main source of instability

Issue 1. Non-orthogonal basis sets

$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \psi_j \middle| \frac{\partial}{\partial t} \middle| \psi_k \right\rangle = \frac{1}{2dt}\begin{pmatrix}\langle \psi_j(r,t) | \psi_k(r,t+dt)\rangle - \langle \psi_j(r,t) | \psi_{\boldsymbol{k}}(r,t)\rangle \\ +\langle \psi_j(r,t+dt) | \psi_k(r,t+dt)\rangle - \langle \psi_j(r,t+dt) | \psi_k(r,t)\rangle\end{pmatrix}$$

Akimov et al., ***JCTC*.** 2016, 12, 5719

Revisit HST Equation

HST Equation

$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \psi_j \middle| \frac{\partial}{\partial t} \middle| \psi_k \right\rangle = \frac{1}{2dt}\left(\langle \psi_j(r,t) | \psi_k(r,t+dt)\rangle - \langle \psi_j(r,t+dt) | \psi_k(r,t)\rangle\right)$$

Main source of instability

Issue 2. Phase inconsistence **determined by the diagonalization routine; basically, it's random**

$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \psi_j \middle| \frac{\partial}{\partial t} \middle| \psi_k \right\rangle = \frac{1}{2dt}\left(\langle \psi_j(r,t) | \psi_k(r,t+dt)\rangle - \langle \psi_j(r,t+dt) | \psi_k(r,t)\rangle\right) \quad \approx \frac{1}{dt}\langle \psi_j(r,t) | \psi_k(r,t+dt)\rangle$$

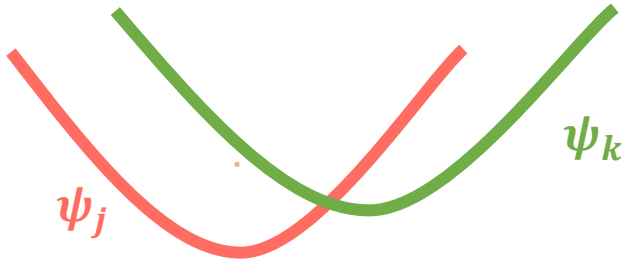
Sign	+1	+1	-1	-1	NAC's sign maybe wrong
Sign	+1	-1	-1	-1	≈ 0

For real wavefunction, you have 25% possibility to get a correct NAC

For complex wavefunction, you have almost zero possibility to get a correct NAC

Revisit HST Equation

Issue 3. Trivial Crossing / Unavoided Crossing



$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \psi_j \middle| \frac{\partial}{\partial t} \middle| \psi_k \right\rangle = \frac{1}{2dt}\left(\langle \psi_j(r,t) | \psi_k(r,t+dt)\rangle - \langle \psi_j(r,t+dt) | \psi_k(r,t)\rangle\right)$$

In reality

$$\frac{1}{2dt}\left(\langle \psi_j(r,t) | \psi_k(r,t+dt)\rangle - \langle \psi_j(r,t+dt) | \psi_k(r,t)\rangle\right) \approx \frac{1}{dt}$$

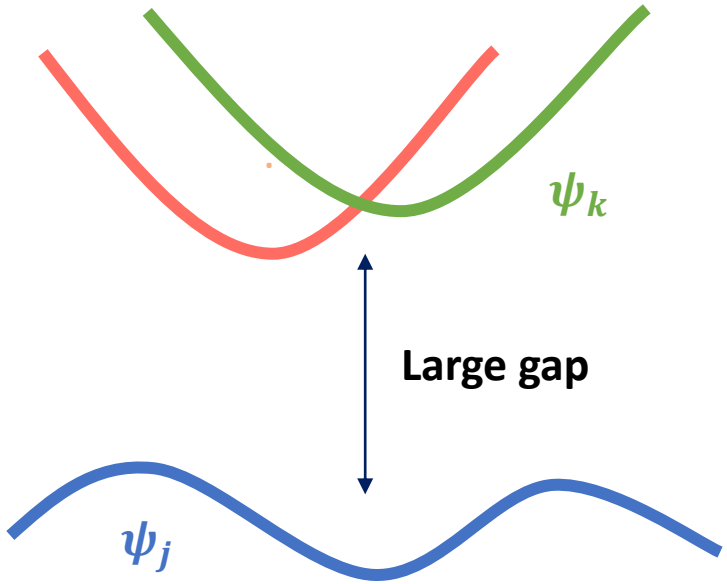
$$\boldsymbol{d_{jk}} \cdot \dot{\boldsymbol{R}} = \left\langle \psi_j \middle| \frac{\partial}{\partial t} \middle| \psi_k \right\rangle = \frac{1}{2dt}\left(\langle \psi_j(r,t) | \psi_k(r,t+dt)\rangle - \langle \psi_j(r,t+dt) | \psi_k(r,t)\rangle\right)$$

In reality

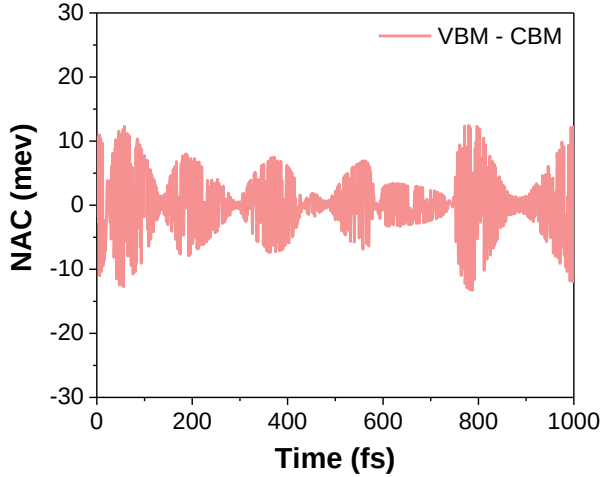
$$\frac{1}{2dt}\left(\langle \psi_j(r,t) | \psi_k(r,t+dt)\rangle - \langle \psi_j(r,t+dt) | \psi_k(r,t)\rangle\right)$$

Phase issue

Spikes for interband relaxation!



Revisit HST Equation



A single issue has limited impact, but putting these problems together may magnify the error several hundred times

Issue 1. Non-orthogonal basis sets

Solution Use orthogonal basis sets

Issue 2. Phase inconsistence

Solution Phase correction

Akimov, *JPCL* **2018**, 9, 6096–6102

Rely on overlap $\langle \psi_j(t) | \psi_j(t+dt) \rangle$

Issue 3. Trivial Crossing / Unavoided Crossing

Solution State tracking

Tretiak et al., JCP **2012**, 137, 10

Rely on overlap $\langle \psi_j(t) | \psi_k(t+dt) \rangle$

Error in pseudo overlap are much larger ~5% to 30%

CAnac can helps!

Code available : https://github.com/WeibinChu/CA-NAC

Acknowledgement

Advisors:

Prof. Oleg Prezhdo	Univ of Southern California (Postdoc advisor)
Prof. Jin Zhao	Univ of Science & Technology of China (PhD advisor)

Collaborators:

Prof. Wissam Saidi	Univ of Pittsburgh
Prof. Alexey Akimov	Univ at Buffalo

Thank You!

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Apr 28th 2021