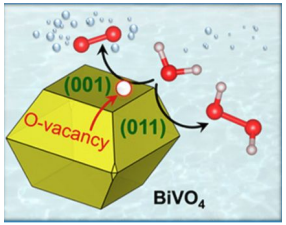
Aperiodic Fragments in Periodic Solids

Rob Lavroff, Daniel Kats, Lorenzo Maschio, Nikolay Bogdanov, Ali Alavi, Anastassia Alexandrova, and Denis Usvyat

VISTA Seminar, 9/18/2024

Defects in solids: a playground for all kinds of chemistry

- Catalysis active sites:
  - Oxygen vacancies in metal-oxide catalysts promote thermal and photocatalysis
  - Single-atom dopants (ie gr-N4 + TM) are at the forefront of electrocatalysis



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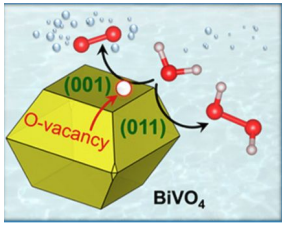
  - NV centers in diamond and silicon as sensors and spin qubits
  - Carbon dopants in hBN as SPEs for quantum communication



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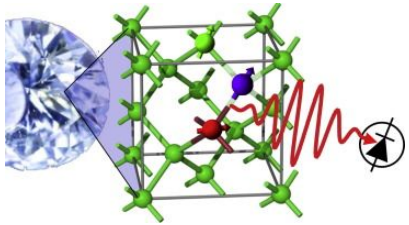

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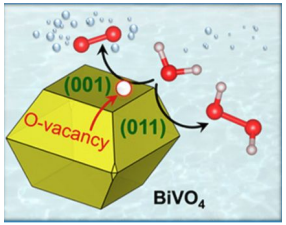
- Clean energy:
  - Tuning transport in batteries and semiconductors via defect engineering
  - Defects as anchoring sites in fuel cells



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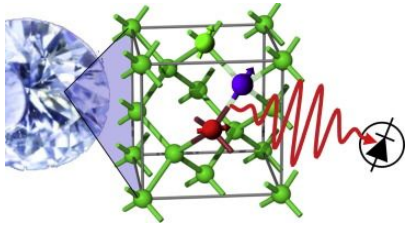

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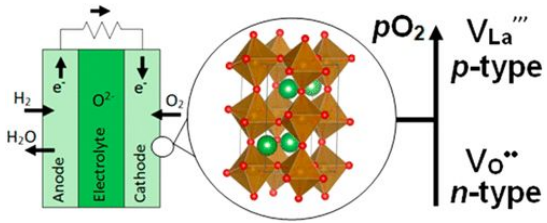

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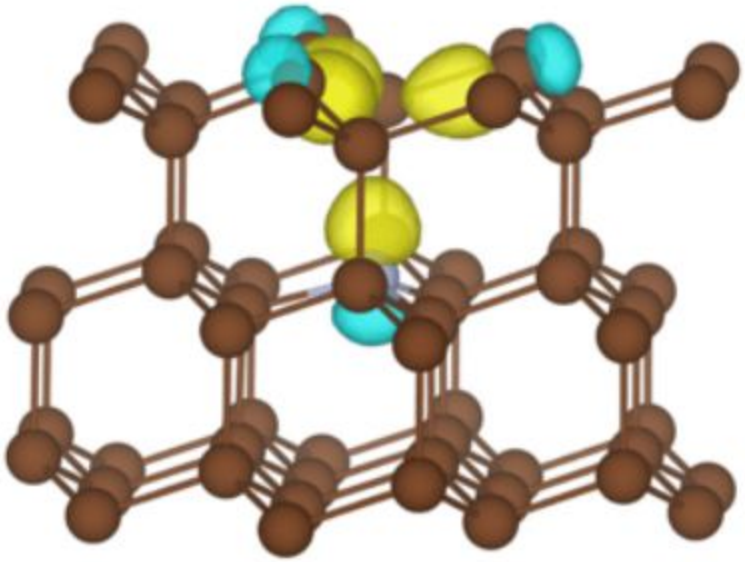
The role of theory in defect chemistry

- Ab-initio calculations can circumvent trial-and-error experiments
  - Binding energies, excited states, spin-couplings, dynamics, etc etc
  - Insights often inaccessible or difficult to obtain via experiment: direct wavefunction information

PhysRevB.105.235104



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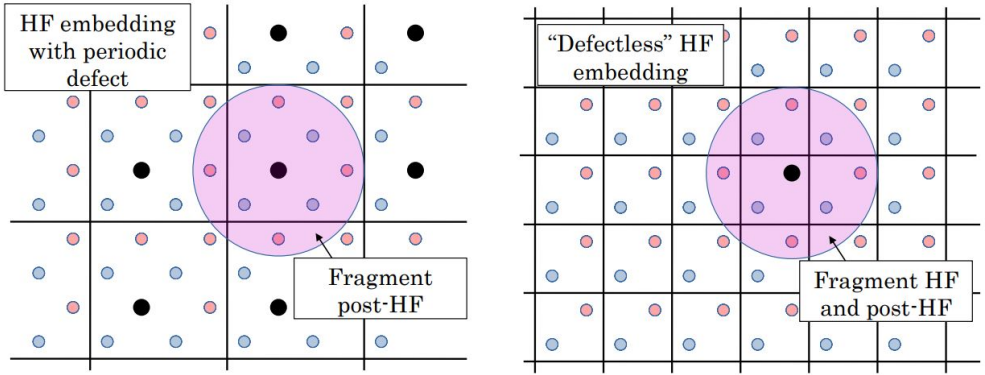
  - Binding energies, excited states, spin-couplings, dynamics, etc etc
  - Insights often inaccessible or difficult to obtain via experiment: direct wavefunction information
- But can current models always give an accurate picture of defects?
  - Relies on periodic boundary conditions, defect is always repeated across unit cells
  - Defects can be spaced at nano- or microscale, routine DFT unit cells < a few nanometers
  - Wavefunction methods (MP2, CC) are more trustworthy, but much smaller unit cells required
  - If a defect is charged (i.e. NV^- center in diamond), need to throw out diverging terms
- The ever-evolving field of **quantum embedding**
  - Can treat defects with near-exact wavefunction methods, pair to cheaper surroundings
  - Suffers from same issue of defect repetition in PBC…

A quantum embedding approach without defect repetition

- Introducing an “aperiodic fragment” approach for the defect could
  - Allow the solid’s unit cell used to be only large enough to house the defect -> **savings**
  - Eliminate the term removal of “compensating background charges” -> **trustworthiness**
  - Assure that defects in different unit cells aren’t artificially interacting -> **accuracy**



arXiv:2406.03373

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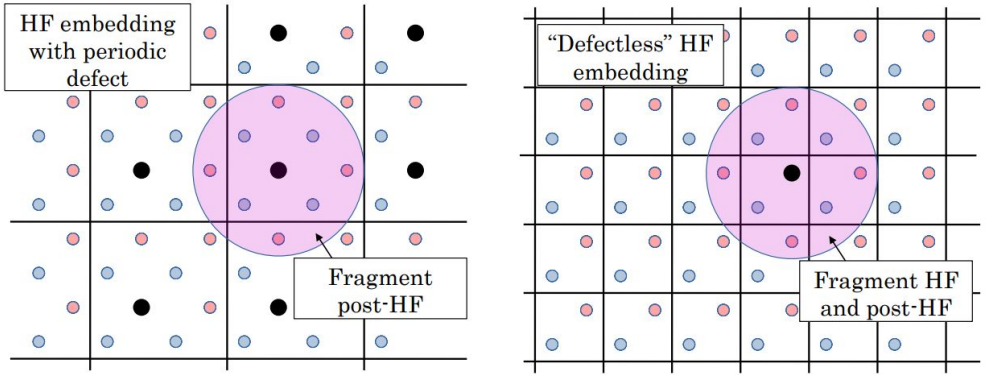
- This approach would need to
  - Converge to the same properties as the periodic approach in the thermodynamic limit (TDL)
  - Take into account the relaxation of the environment due to the defect
  - Have flexibility in ab-initio approaches to tackle a variety of defects



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Aperiodic fragment in frozen mean-field surroundings

- Embedding often uses HF for surroundings: no double counting of E_{corr}
  - Self-consistency or expansion of correlated fragment fixes lack of correlation later
- Fragment HF energy same form as a molecule's, but with modified h and E_{nuc}

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&+ \sum_{K'\in\mathrm{frag}} Z_{K'}\cdot V\left(\mathbf{R}_{K'}\right) \\
&+2\sum_{i\in\mathrm{frag}}\left\langle i\left|\sum_{K'\in\mathrm{frag}}\frac{Z_{K'}}{|\mathbf{r}-\mathbf{R}_{K'}|}\right|i\right\rangle - \sum_{L\in\mathrm{frag}}\sum_{K'\in\mathrm{frag}}{}'\frac{Z_L Z_{K'}}{|\mathbf{R}_L-\mathbf{R}_{K'}|}.
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μ', ν' , ...: fragment's basis orbitals; K, L, ...: atoms of the fragment before introduction of the defect; K', L', ...: atoms of the fragment after introduction of the defect; i, j, ...: the occupied orbitals before the fragment's SCF; i' , j', ...: the occupied orbitals after the fragment's SCF; $V(\mathbf{R}_{K'})$: the periodic electrostatic potential at the point $\mathbf{R}_{K'}$

Aperiodic fragment in frozen [redacted] surroundings

- Embedding often uses [redacted] counting of E_{corr}
  - Self-consisten[redacted] correlation later
- Fragme[redacted] modified h and E_{nuc}

In the Fock matrix, we remove the contributions from the pristine crystal inside the fragment and add those of the "defected" crystal, then do SCF

$$E_{\mathrm{HF}}^{\mathrm{frag}} = [\text{redacted}] - \sum_{L\in\mathrm{frag}}\sum_{K'\in\mathrm{frag}} \frac{Z_L Z_{K'}}{|\mathbf{R}_L - \mathbf{R}_{K'}|}$$

$$= F_{\mu'\nu'}^{\mathrm{per}} - \sum_{i\in\mathrm{frag}} \left[2\,(\mu'\nu'|ii) - (\mu' i|i\nu')\right] + \sum_{K\in\mathrm{frag}} \left\langle \mu' \left| \frac{Z_K}{|\mathbf{r}-\mathbf{R}_K|} \right| \nu' \right\rangle - \sum_{K'\in\mathrm{frag}} \left\langle \mu' \left| \frac{Z_{K'}}{|\mathbf{r}-\mathbf{R}_{K'}|} \right| \nu' \right\rangle$$

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Aperiodic fragment in frozen mean-field surroundings

- Embedding often … surroundings: no double counting of E_{corr}
  - Self-consistency … fragment fixes lack of correlation later
- Fragment HF energy … but with modified h and E_{nuc}

In the total energy we remove the environment:pristine-fragment interactions and add the environment:"defected"-fragment interactions

$$E_{\mathrm{HF}}^{\mathrm{frag}} = 2\sum_{i'\in\mathrm{frag}} h_{i'i'}^{\mathrm{frag}} + \frac{1}{2}\sum_{i'\in\mathrm{frag}}\sum_{j'} \ldots \left\langle \ldots \left| \sum \frac{Z_{K'}}{|\mathbf{r}-\mathbf{R}_{K'}|} \right| \nu' \right\rangle$$

$$+\frac{1}{2}\sum_{K'\in\mathrm{frag}}\sum_{L'\in\mathrm{frag}}{}' \frac{Z_{K'}}{|\mathbf{R}_{K'}-\mathbf{R}_{L'}|} \ldots - (\mu' i|i\nu')]$$

$$+\sum_{K'\in\mathrm{frag}} Z_{K'}\cdot V(\mathbf{R}_{K'})$$

$$+2\sum_{i\in\mathrm{frag}}\left\langle i\left|\sum_{K'\in\mathrm{frag}}\frac{Z_{K'}}{|\mathbf{r}-\mathbf{R}_{K'}|}\right|i\right\rangle - \sum_{L\in\mathrm{frag}}\sum_{K'\in\mathrm{frag}}{}'\frac{Z_L Z_{K'}}{|\mathbf{R}_L-\mathbf{R}_{K'}|}.$$

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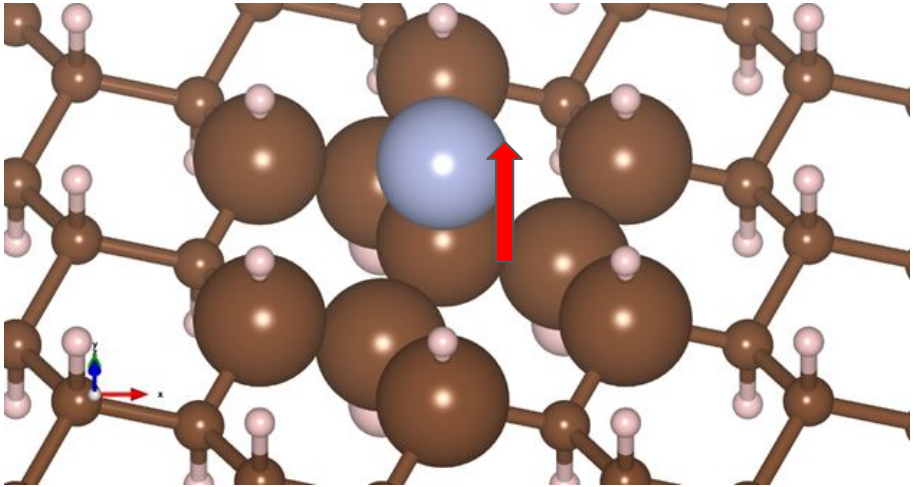
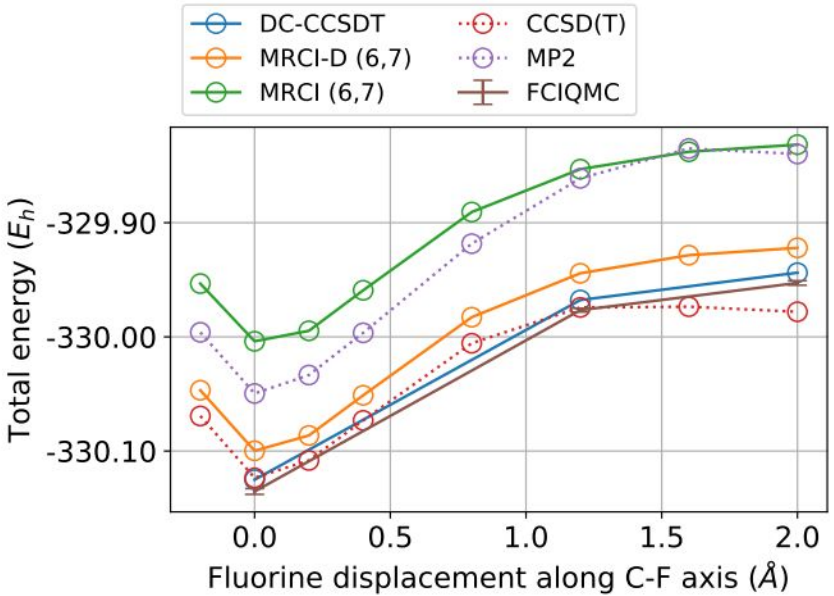
Putting things to the test: Fluorographane

- Real material (10.1038/s41565-019-0582-z) and an interesting testing ground
- Substitute a H in graphane with a F, then start breaking the C-F bond
  - As bond is stretched, static correlation increases, dynamic correlation of F valence electrons



Periodic embedding vs aperiodic



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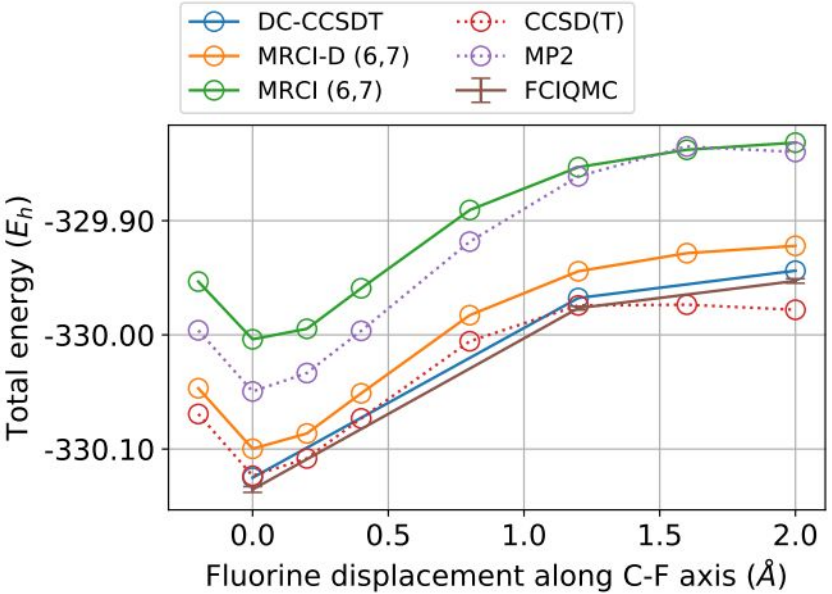
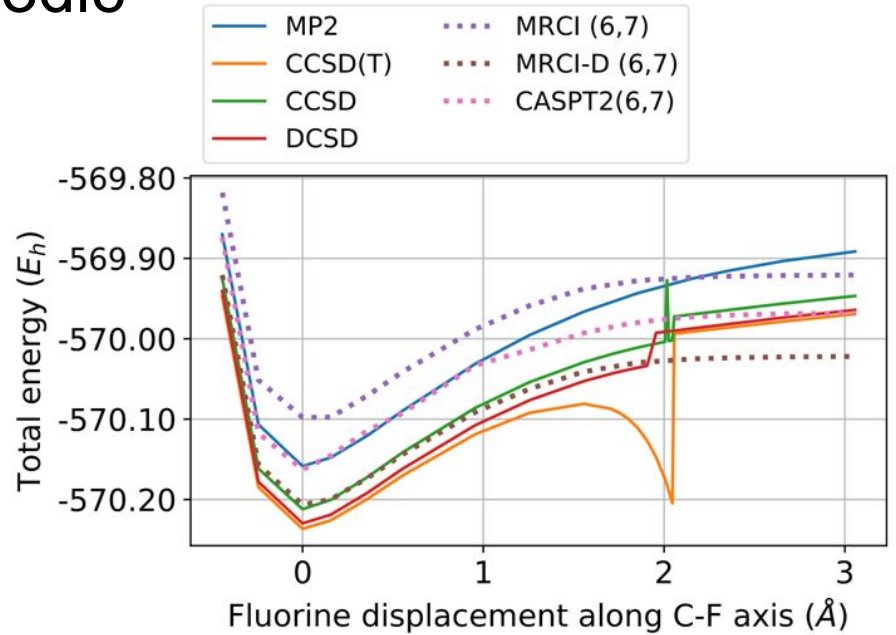
  - 10.1063/5.0084040
- Expected behavior of MP2 and CCSD(T) in strong correlation

Periodic embedding vs aperiodic





- Old, periodic scheme (2x2 supercell)
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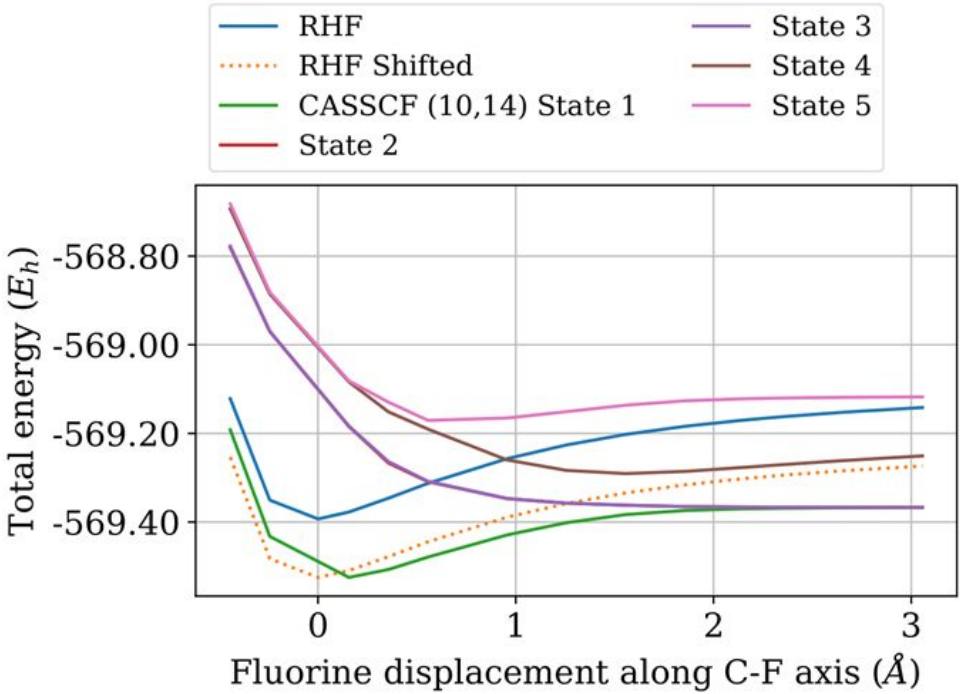
- Expected behavior of MP2 and CCSD(T) in strong correlation

- Aperiodic approach, same 14-atoms
- MP2 behaves like HF, CC/DC has major issues at 2Å but like MP2 after
  - An avoided crossing?

A crossing! Does aperiodic reproduce periodic in the TDL?



Using aperiodic embedding, RHF zips along a covalent-ionic crossing (follows ionic diabat)

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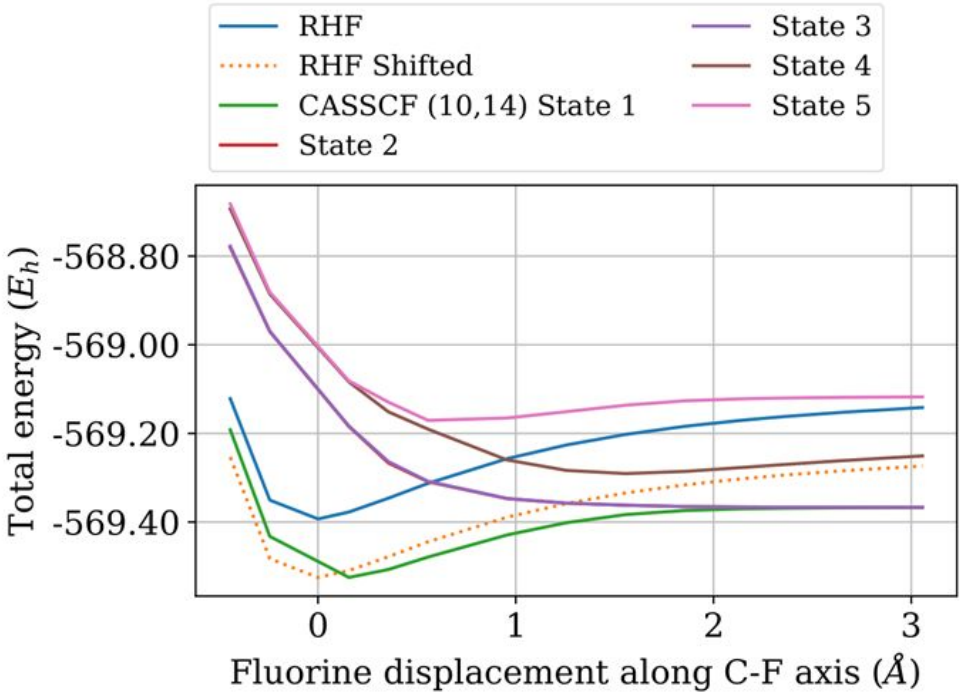
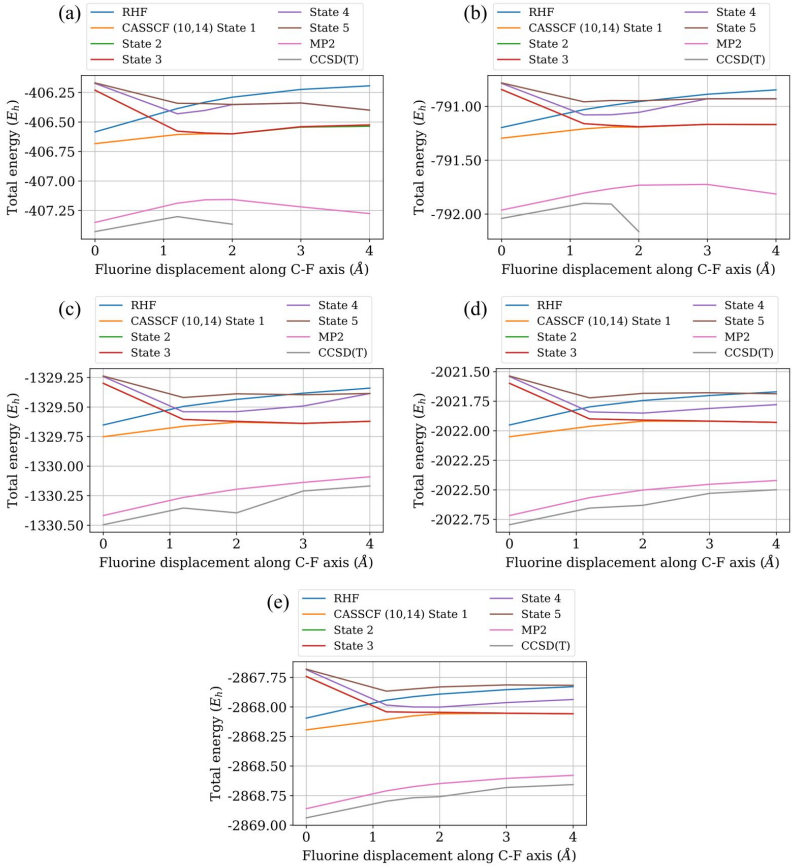
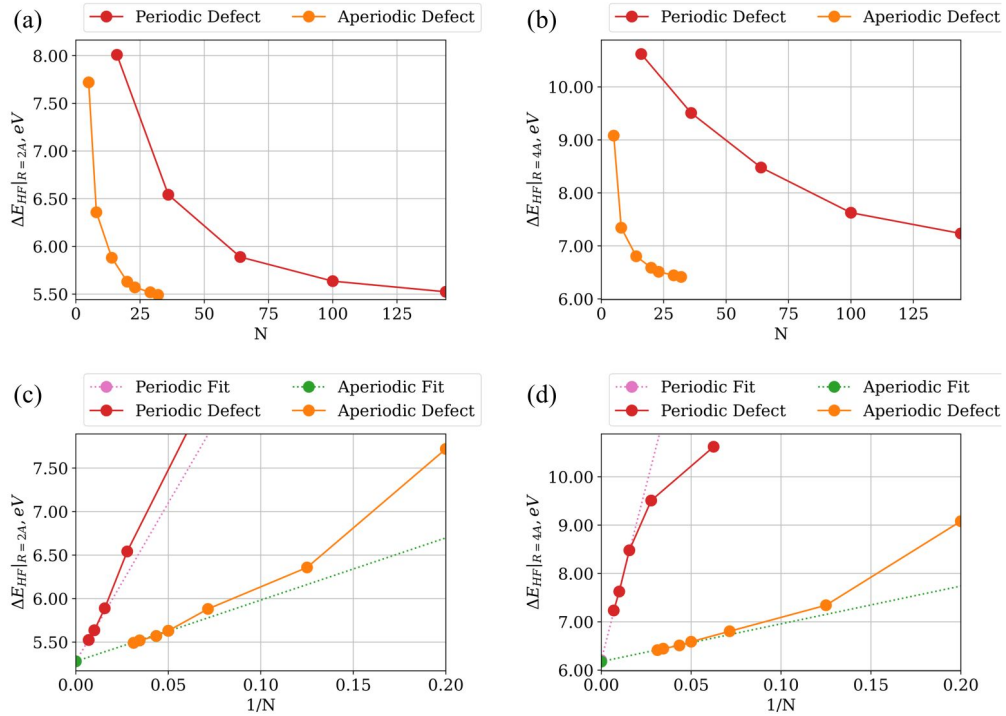




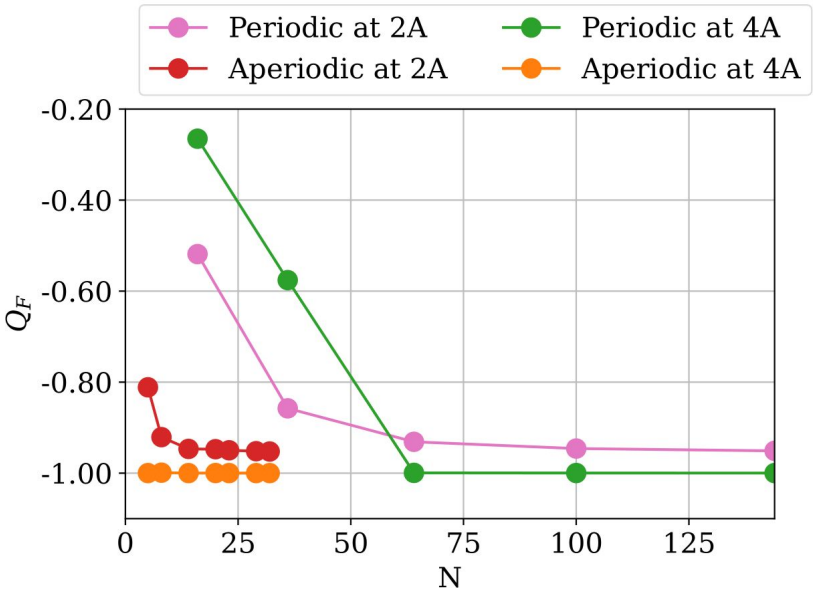
As we take periodic scheme from 2x2 to 6x6, excited state manifold (and MP2/CC) match!

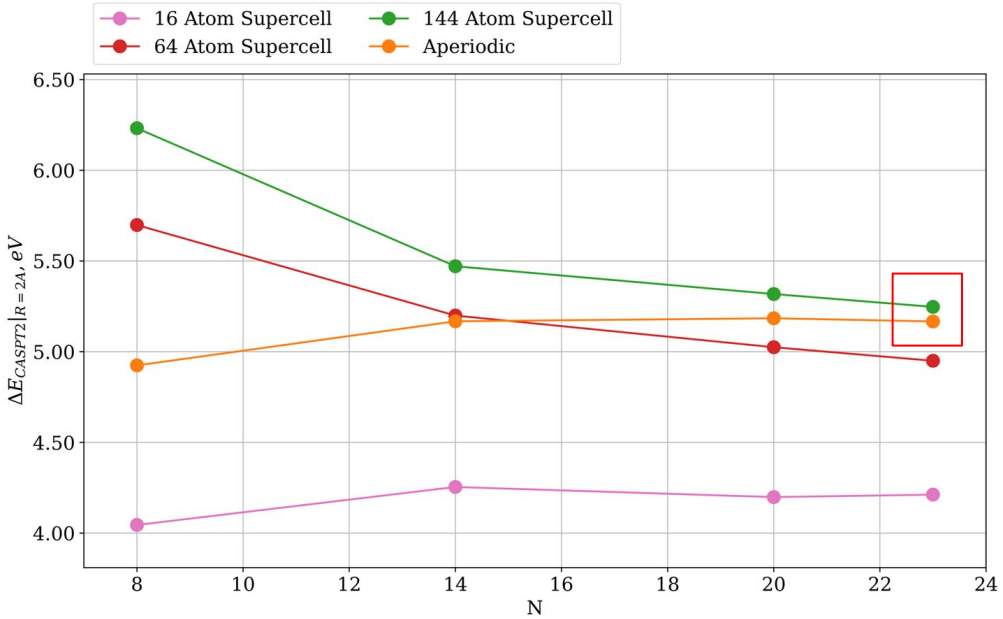
What about quantitative agreement in the TDL?

- HF dissociation energy at bond displacements of 2 and 4 A at N atoms
- At large enough fragments/supercells, a linear regime in 1/N begins: exact match



HF Mulliken F Charge and CASPT2 Dissociation Energies





For CASPT2, an embedded fragment must be used for periodic too, so N=number of atoms in fragment

Conclusions and next steps

- Aperiodic embedding can:
  - Give correct ground and excited state PES using a minimal unit cell, while periodic can require very large supercells to get here
  - Converge to the same TDL values of dissociation energies and Mulliken charges as periodic
    - Periodic is over 400x more costly for this 2-D system
  - Capture response of the environment in this system by simply expanding the fragment
    - HF’s ionic dissociation induces a large dipole, yet TDL properties match fully periodic ones

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  - Capture response of the environment in this system by simply expanding the fragment
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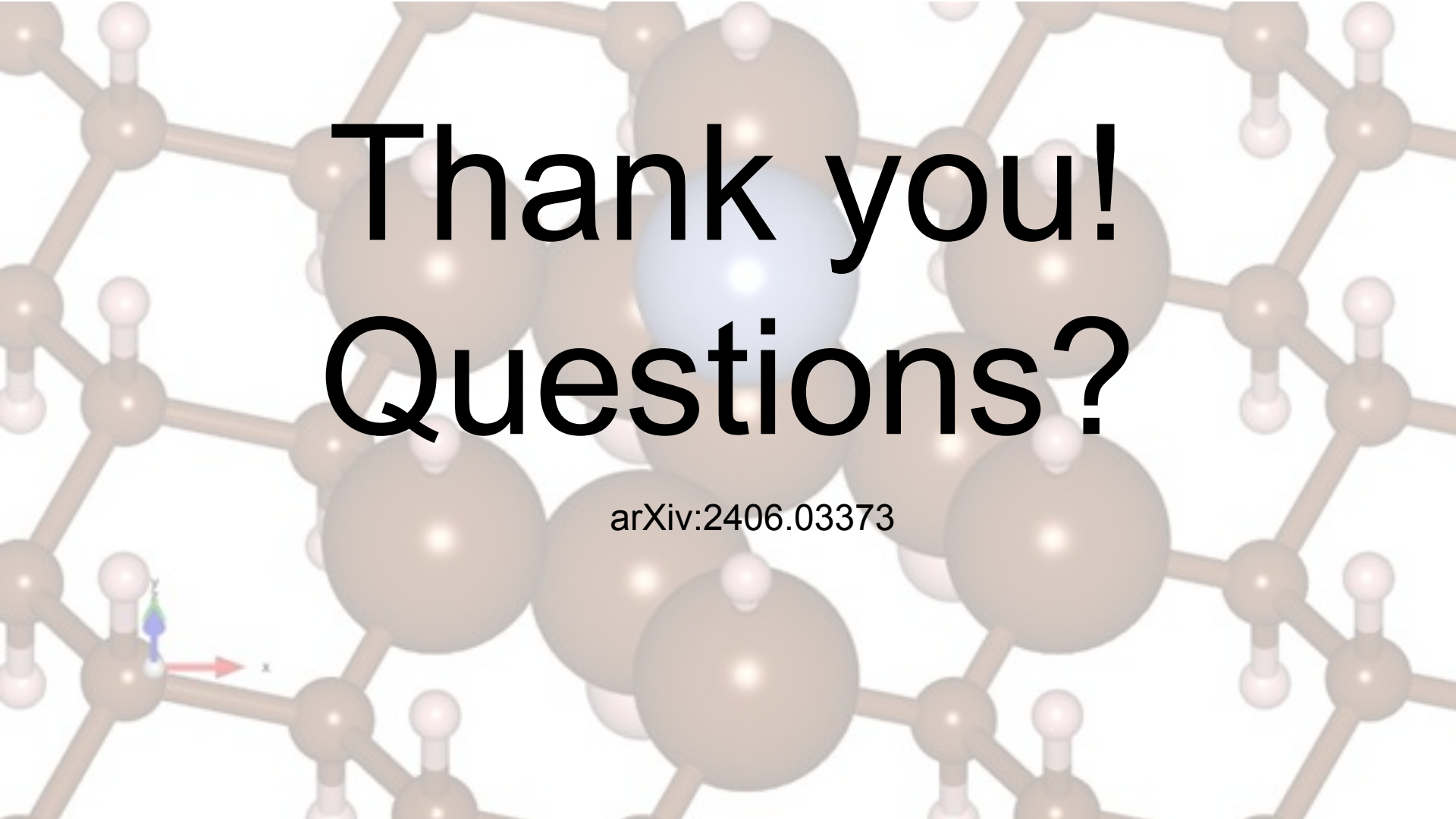
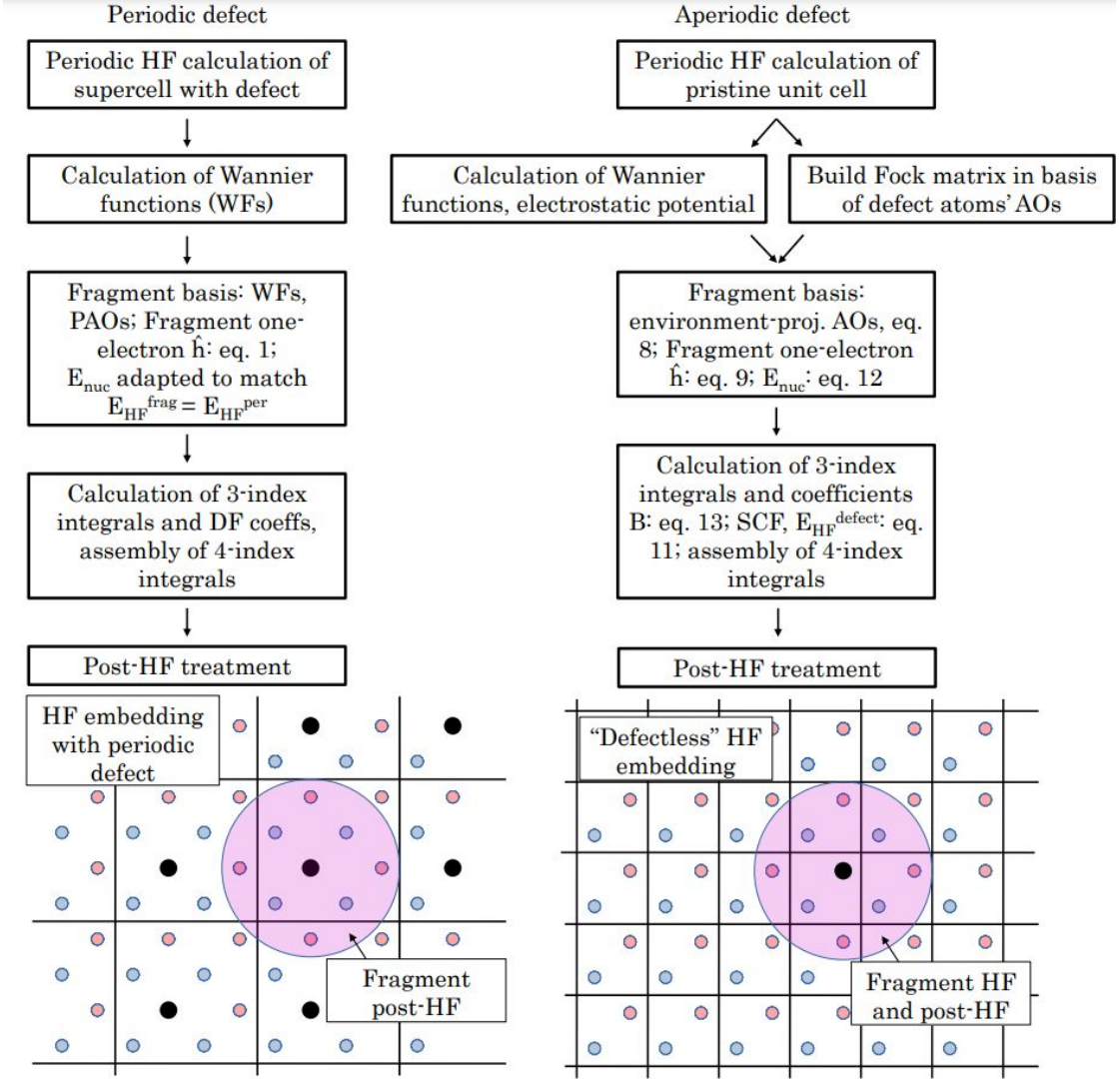
- Future steps/works in progress:
  - Testing on charged systems and defects in 3-D crystals (is the speedup even greater?)
  - Analytic gradients of the fragment HF energy: fast geometry optimizations of defects
  - Computing SOCs and NACs: heavy atoms and nonadiabatic dynamics of defects
  - Self-consistency between fragment and environment to allow smaller fragments
    - Applying the approach to metals - fragment is an open system


Thank you!
Questions?
arXiv:2406.03373

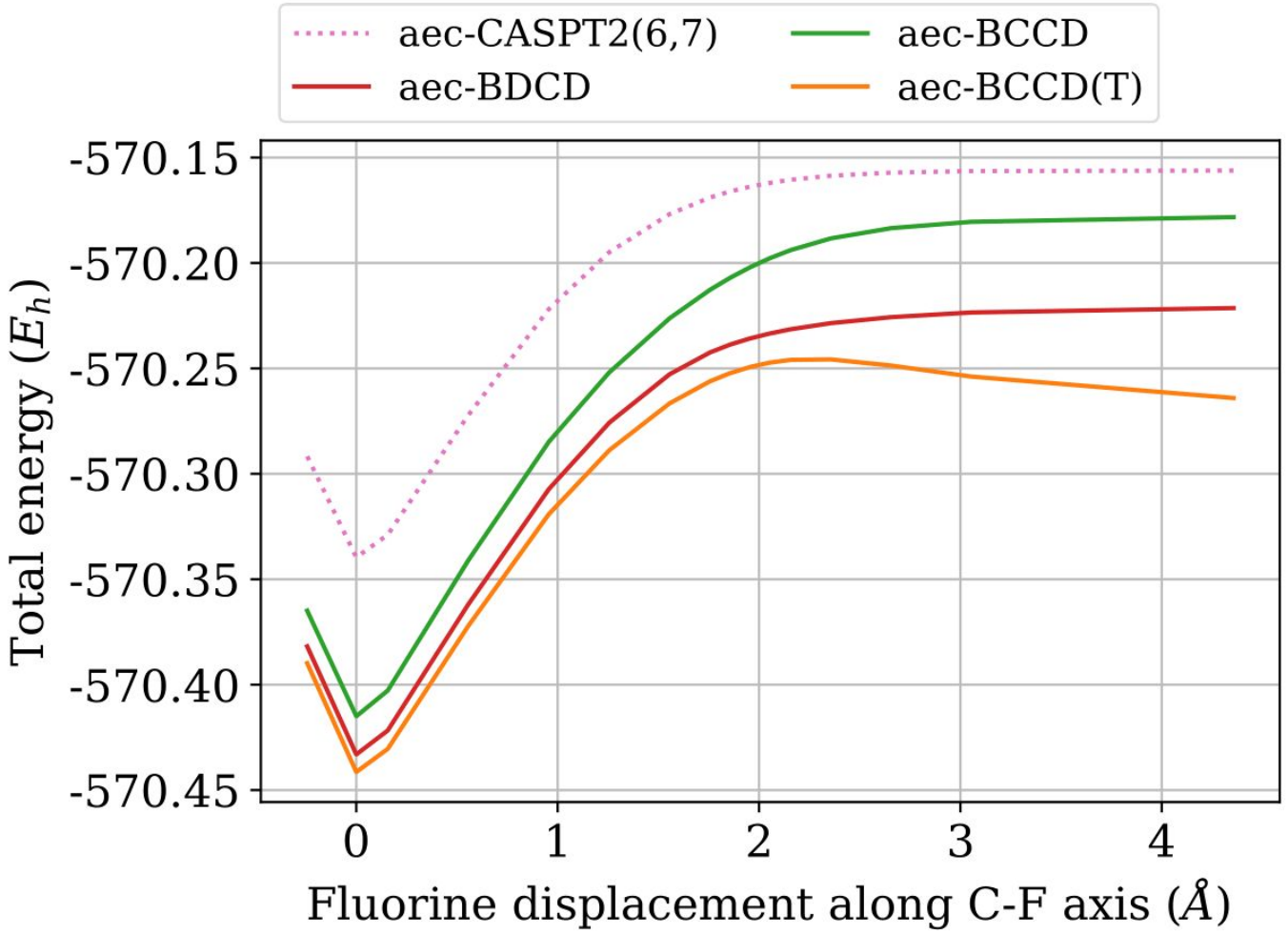
Workflow


Periodic defect
Periodic HF calculation of supercell with defect
Calculation of Wannier functions (WFs)
Fragment basis: WFs, PAOs; Fragment one-electron ĥ: eq. 1; E_{nuc} adapted to match $E_{HF}^{frag} = E_{HF}^{per}$
Calculation of 3-index integrals and DF coeffs, assembly of 4-index integrals
Post-HF treatment
HF embedding with periodic defect
Fragment post-HF
Aperiodic defect
Periodic HF calculation of pristine unit cell
Calculation of Wannier functions, electrostatic potential
Build Fock matrix in basis of defect atoms' AOs
Fragment basis: environment-proj. AOs, eq. 8; Fragment one-electron ĥ: eq. 9; E_{nuc}: eq. 12
Calculation of 3-index integrals and coefficients B: eq. 13; SCF, E_{HF}^{defect}: eq. 11; assembly of 4-index integrals
Post-HF treatment
"Defectless" HF embedding
Fragment HF and post-HF

Definition of the electrostatic potential and E_{per}^{HF}

$$Z_K \left[-2 \sum_i \left\langle i \left| \frac{1}{|\mathbf{r} - \mathbf{R}_K|} \right| i \right\rangle + \sum_L{}' \frac{Z_L}{|\mathbf{R}_K - \mathbf{R}_L|} \right]$$
$$= Z_K \cdot V(\mathbf{R}_K)$$

$$\begin{aligned} E_{\mathrm{HF}}^{\mathrm{per}} &= 2 \sum_{i \in \mathrm{cell}} h_{ii} + \sum_{i \in \mathrm{cell}} \left(2J_{ii}^{\mathrm{per}} - K_{ii}^{\mathrm{per}} \right) + E_{\mathrm{nuc}}^{\mathrm{per}} \\ &= 2 \sum_{i \in \mathrm{cell}} \left\langle i \left| -\tfrac{1}{2} \nabla^2 \right| i \right\rangle + 2 \sum_{i \in \mathrm{cell}} \left\langle i \left| - \sum_K \frac{Z_K}{|\mathbf{r} - \mathbf{R}_K|} \right| i \right\rangle \\ &\quad + \sum_{i \in \mathrm{cell}} \sum_j [2(ii|jj) - (ij|ji)] + \tfrac{1}{2} \sum_{K \in \mathrm{cell}} \sum_L \frac{Z_K Z_L}{|\mathbf{R}_K - \mathbf{R}_L|}. \end{aligned}$$


aec-CASPT2(6,7)
aec-BCCD
aec-BDCD
aec-BCCD(T)
-570.15
-570.20
-570.25
-570.30
-570.35
-570.40
-570.45
Total energy (E_h)
0
1
2
3
4
Fluorine displacement along C-F axis ($\AA$)