First-principles diagrammatic simulations of solids

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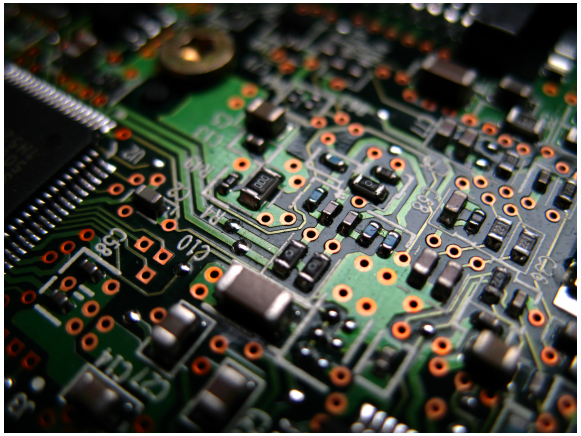
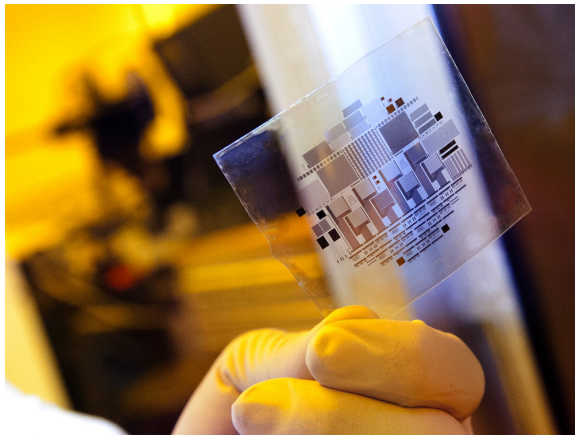
Devices

Digital

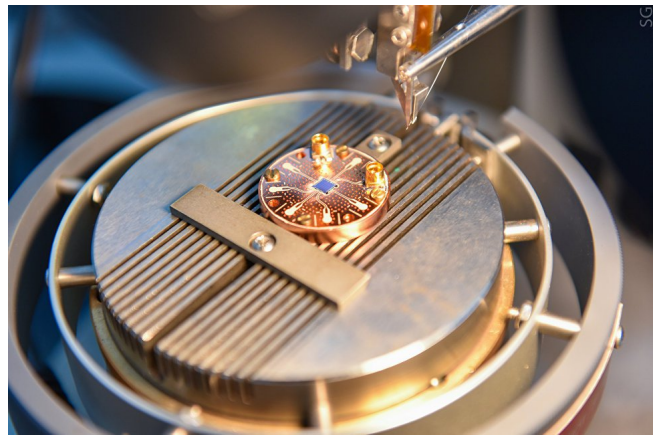


Energy

Bio



Beyond



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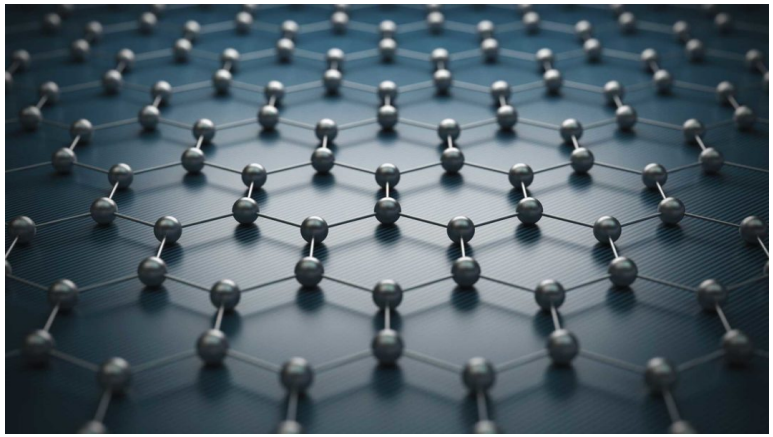
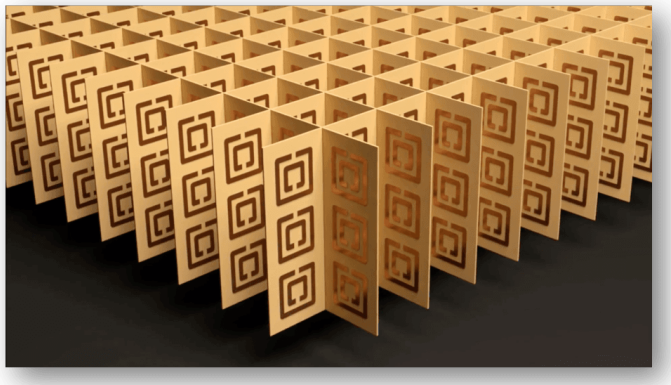
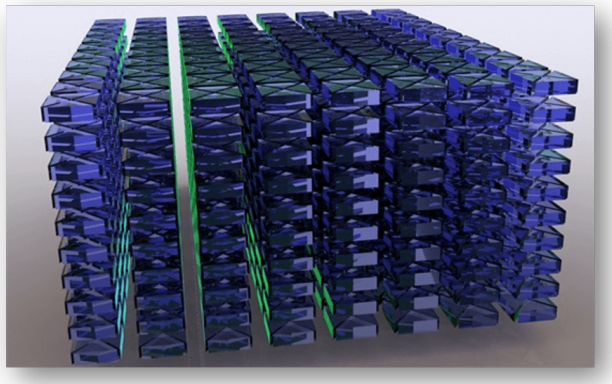
Novel materials

- Two-dimensional



- Metamaterials





- Layered, artificial, organic, ...

Properties

- Electronic
  - band gaps
  - spectral functions
  - light-matter
  - magnetism
  - electronic phases
- Mechanical
  - elastic
  - thermal expansion
  - piezoelectric
- Defects
- Interfaces
- Phases
- Alloys

Materials modeling

Aims:

- Solve the many-body electronic problem numerically

$$H = H_{1\mathrm{p}} + H_{2\mathrm{p}} = -\sum_i \frac{\Delta_i}{2} + U(r_i) + \frac{1}{2}\sum_{ij} \frac{1}{|r_i - r_j|}$$

(fermions, Born-Oppenheimer approximation)

first-principles

- Compare/reference to experimental data

Density functional theory

- Practical perspective:

$$H = H_{1\mathrm{p}} + \cancel{H_{2\mathrm{p}}} + V_{\mathrm{eff},1\mathrm{p}} \quad \rightarrow \text{solved easily}$$

- $V_{\mathrm{eff},1\mathrm{p}}[\rho]$ fitted to simple models / experimental data
- A special role of density ρ: mean-field approximation

Pros:

- Fast $\rightarrow$ enables calculations of larger/more complex models;
- Lots of reference data, codes, large community
- Extensible (+U, hybrid, etc.)

Cons:

- No errorbar, no wf, sometimes not variational
- Empiric approach
- Lack of alternatives ...

... Alternatives

- Mean-field
  - DFT — cost of diagonalization – $O(N^3)$
  - Hartree-Fock = DFT with 100% exchange and 0% correlations — # of 2-el integrals (typical) - $O(N^4)$
- Diagrammatic theories
  - *GW* — $O(N^4 - N^6)$
  - perturbation theory (MP2) — $O(N^5+)$
  - configuration interaction (CI) — $O(N^6+)$
  - coupled-cluster (CC) — $O(N^6+)$
- Wavefunction
  - exact — $O(e^{\cdots N})$
  - quantum stochastic — $O(N^3)$*
  - tensor networks — $O(N)$*
- $O(N)$* methods

N - size of the model

Numerical aspects

Second quantization

- Define a finite single-particle basis set
  - real-space grid
  - plane waves
  - atom-centered functions (STO, Gaussians, numerical) $\rightarrow$ **atomic basis**
- Calculate matrix elements h, v

$$H = H_{1p} + H_{2p} = \sum_{\alpha\beta} h_{\alpha\beta} c_\alpha^\dagger c_\beta + \sum_{\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta} c_\alpha^\dagger c_\beta^\dagger c_\delta c_\gamma$$

  α, β, ... are both in "real" and spin-1/2 space

- $v_{\alpha\beta\gamma\delta} = \int dr_1 dr_2 \; \phi_\alpha^*(r_1)\phi_\gamma(r_1)\frac{1}{|r_1 - r_2|}\phi_\beta^*(r_2)\phi_\delta(r_2)$

Hartree-Fock

- Mean-field approximation
- Basis rotation: $\phi_i(r) = \sum_\alpha c_{i\alpha}\phi_\alpha(r)$
- Antisymmetric product

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(\mathbf{r_1}) & \phi_2(\mathbf{r_1}) & \dots & \phi_N(\mathbf{r_1}) \\ \phi_1(\mathbf{r_2}) & \phi_2(\mathbf{r_2}) & \dots & \phi_N(\mathbf{r_2}) \\ & & \dots & \\ \phi_1(\mathbf{r_N}) & \phi_2(\mathbf{r_N}) & \dots & \phi_N(\mathbf{r_N}) \end{vmatrix}$$

- Ansatz:

$$\langle\Psi|H|\Psi\rangle = E_{\mathrm{HF}}\left(c_{i\alpha}\right) \to \min$$

- Unique up to a unitary:

$$E_{\mathrm{HF}}\left(c_{i\alpha}\right) = E_{\mathrm{HF}}\left(\sum_j U_{ij}c_{j\alpha}\right)$$

Hartree-Fock

- $E_{\mathrm{HF}} = \langle \Psi | H | \Psi \rangle =$
  $\sum_{i\alpha\beta} c^*_{i\alpha} c_{i\beta} \cdot h_{\alpha\beta} + \frac{1}{2} \sum_{ij\alpha\beta\gamma\delta} v_{\alpha\beta\gamma\delta} \cdot c^*_{i\alpha} c_{i\gamma} \cdot c^*_{j\beta} c_{j\delta} - v_{\alpha\beta\gamma\delta} \cdot c^*_{i\alpha} c_{i\delta} \cdot c^*_{j\beta} c_{j\gamma} =$
  $\rho_{\alpha\beta} \cdot h_{\alpha\beta} + \frac{1}{2} v_{\alpha\beta\gamma\delta} \cdot \rho_{\alpha\gamma} \cdot \rho_{\beta\delta} - \frac{1}{2} v_{\alpha\beta\gamma\delta} \cdot \rho_{\alpha\delta} \cdot \rho_{\beta\gamma} = E + J - K$
  - E - density in external potential
  - J - density in self-induced potential (Coulomb)
  - K - exchange
- Compare: Hartree (direct) product $|\Psi\rangle = \prod_i \phi_i(\mathbf{r_i})$:

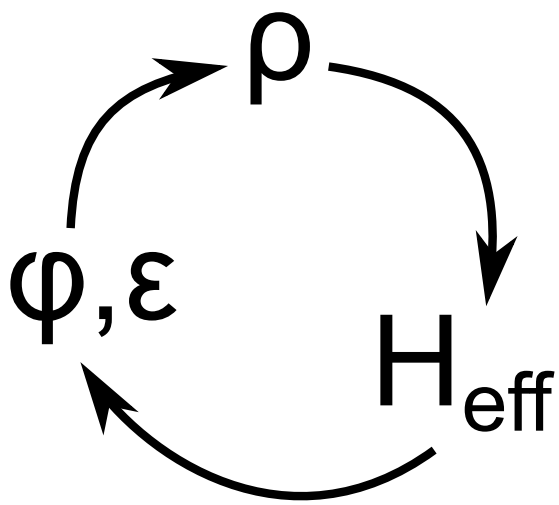
$$E_{\mathrm{H}} = \langle \Psi | H | \Psi \rangle = E + J > E_{\mathrm{HF}}$$

- DFT view:

$$E_{\mathrm{HF}} = \rho_{\alpha\beta} \left[h_{\alpha\beta} + \frac{1}{2} \left(v_{\alpha\gamma\beta\delta} - v_{\alpha\gamma\delta\beta} \right) \cdot \rho_{\gamma\delta} \right] = \rho_{\alpha\beta} \left(h_{\alpha\beta} + V^{\mathrm{eff}}_{\alpha\beta}[\rho] \right)$$

Self-consistency

Constrain $c_{i\alpha} \rightarrow$ eigenvectors of $h_{\alpha\beta} + V^{\text{eff}}_{\alpha\beta}[\rho]$ with lowest eigenvalues ϵ_i

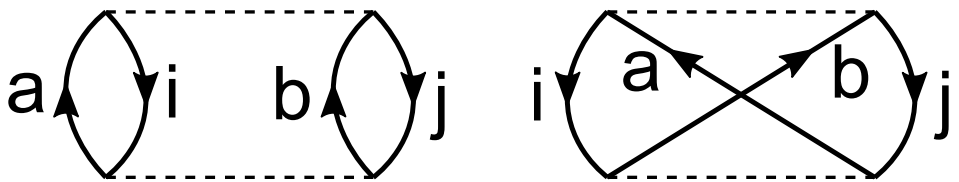


Perturbations

1. HF $\rightarrow$ occupied, virtual ϕ
2. Rotate H into ϕ:

   $H_{1\mathrm{p}} + H_{2\mathrm{p}} =$
   $\left(h_{ij} \cdot \mathbf{c_i}^\dagger \mathbf{c_j} + h_{ia} \cdot \mathbf{c_i}^\dagger \mathbf{c_a} + h_{ai} \cdot \mathbf{c_a}^\dagger \mathbf{c_i} + h_{ab} \cdot \mathbf{c_a}^\dagger \mathbf{c_b}\right)_1 + \left(v_{ijkl} \cdot \mathbf{c_i}^\dagger \mathbf{c_j}^\dagger \mathbf{c_l} \mathbf{c_k} + \ldots\right)_2$,
   $ijkl\ldots$ - occupied space, $abcd\ldots$ - virtual space
3. Define new vacuum $|0\rangle := |\Phi\rangle$
4. Use symmetry, qp vacuum (normal ordering), ... to calculate perturbation terms

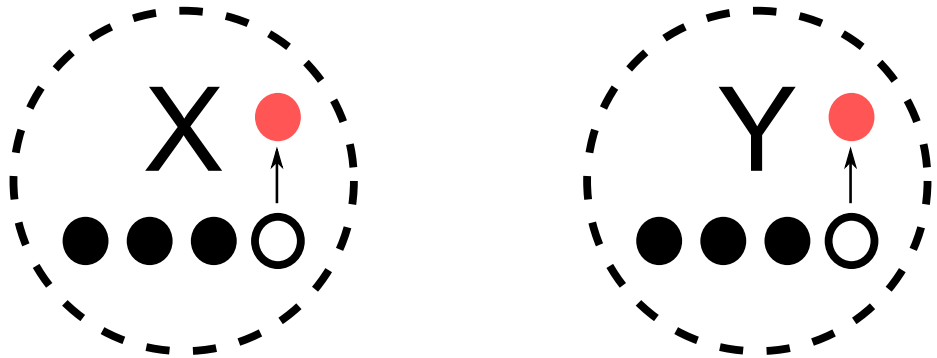
$$E_{\mathrm{MP2}} = \sum_{\Phi} |\langle \Phi | H - H_{\mathrm{HF}} | \Psi \rangle|^2 / \left(E_\Psi - E_\Phi\right) = -\frac{1}{4} \sum_{ijab} \frac{v \cdot v - v \cdot v}{\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j}$$



The many-body state

- Define determinant basis $\mathbf{c_a}^\dagger \mathbf{c_b}^\dagger \mathbf{c_c}^\dagger ... \mathbf{c_i c_j c_k} ... \left|0\right\rangle$, $i < j < k < ... < a < b < c < ...$
- $T = \sum_{ia} t_i^a \cdot \mathbf{c}_a^\dagger \mathbf{c}_i + \sum_{ijab} t_{ij}^{ab} \cdot \mathbf{c}_a^\dagger \mathbf{c}_b^\dagger \mathbf{c}_i \mathbf{c}_j + ...$ - particle-conserving excitations
- $(1 + T)\left|0\right\rangle$ - a many-body state in terms of amplitudes t (not normalized)

Size consistency



CI ansatz:

$$\Psi_X = (1 + T_X)\,|0\rangle_X\,; \quad \Psi_Y = (1 + T_Y)\,|0\rangle_Y\,:$$

$$\Psi_{X+Y} = (1 + T_X)\,|0\rangle_X \times (1 + T_Y)\,|0\rangle_Y = (1 + T_X + T_Y + T_X T_Y)\,|0\rangle_{XY}$$

Coupled-cluster (CC) ansatz

$$\Psi = e^T\,|0\rangle\,: \quad \Psi_{X+Y} = e^{T_X}\,|0\rangle_X \times e^{T_Y}\,|0\rangle_Y = e^{T_X+T_Y}\,|0\rangle_{XY}$$

CC equations

Variational ansatz

$$E = \left\langle 0 \middle| e^{T^\dagger} H e^{T} \middle| 0 \right\rangle$$

- e^{T} - infinite excitations (creates particle-hole pairs)
- $e^{T^\dagger}$ - infinite annihilations;

"Infinite" number of terms

Instead, use the eigenvalue approach

$$e^{-T} H e^{T} |0\rangle = E |0\rangle$$

CC equations

For approximate T (i.e. single, double excitations) $T = T_1 + T_2$:

$$e^{-T_1-T_2} H e^{T_1+T_2} |0\rangle \neq E |0\rangle \leftarrow \text{overdefined}$$

Fix the number of equations to match the number of parameters by projecting onto CI space

$$P = |0\rangle\langle 0| + \sum_{ia} \left|{}^{a}_{i}\right\rangle\left\langle{}^{a}_{i}\right| + \sum_{ijab} \left|{}^{ab}_{ij}\right\rangle\left\langle{}^{ab}_{ij}\right|$$

And solve:

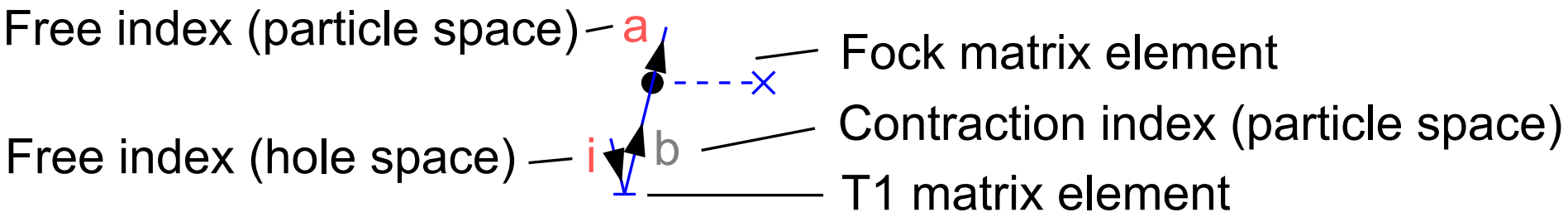
$$P e^{-T_1-T_2} H e^{T_1+T_2} |0\rangle = E |0\rangle$$

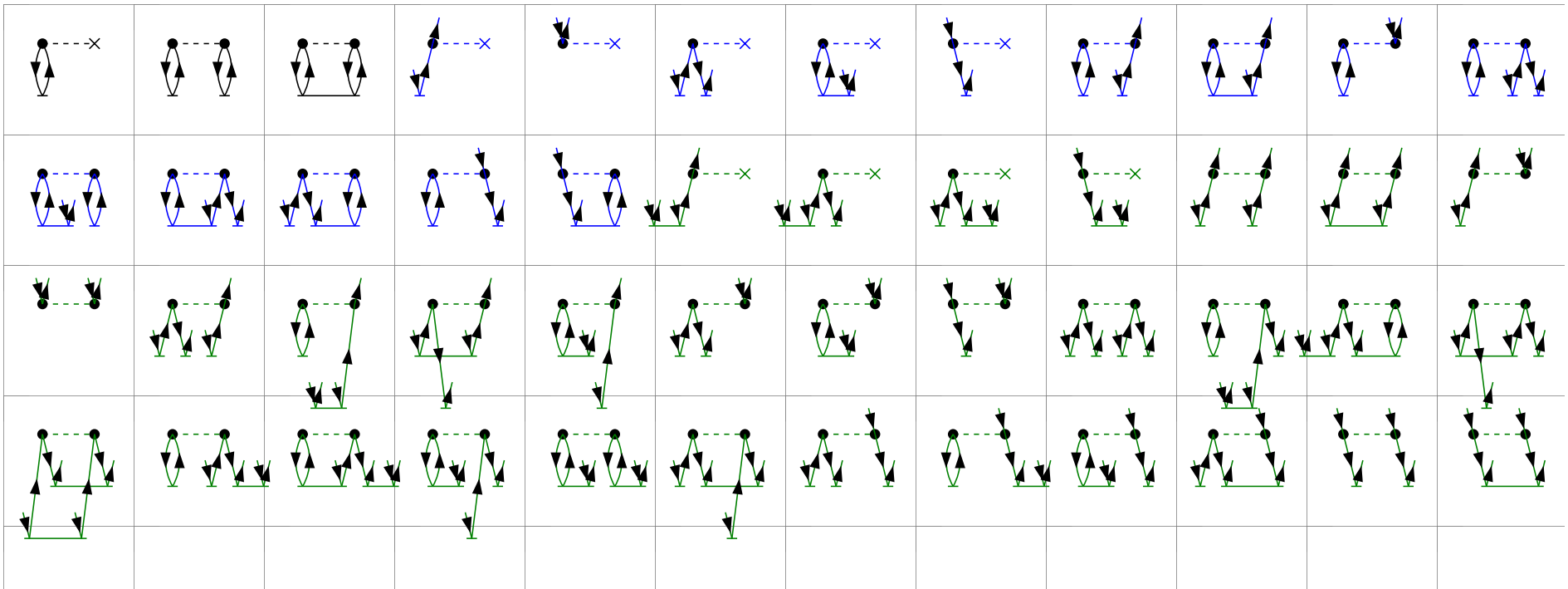
(hoping that you are still targeting the ground state)

CC diagrams

Bookkeeping = diagrams

$$\left\langle \begin{matrix} a \\ i \end{matrix} \middle| e^{-T} H e^{T} \middle| 0 \right\rangle = \sum_b f_{ab} T_i^b + f_{ai} + \ldots$$





Benchmark: diamond

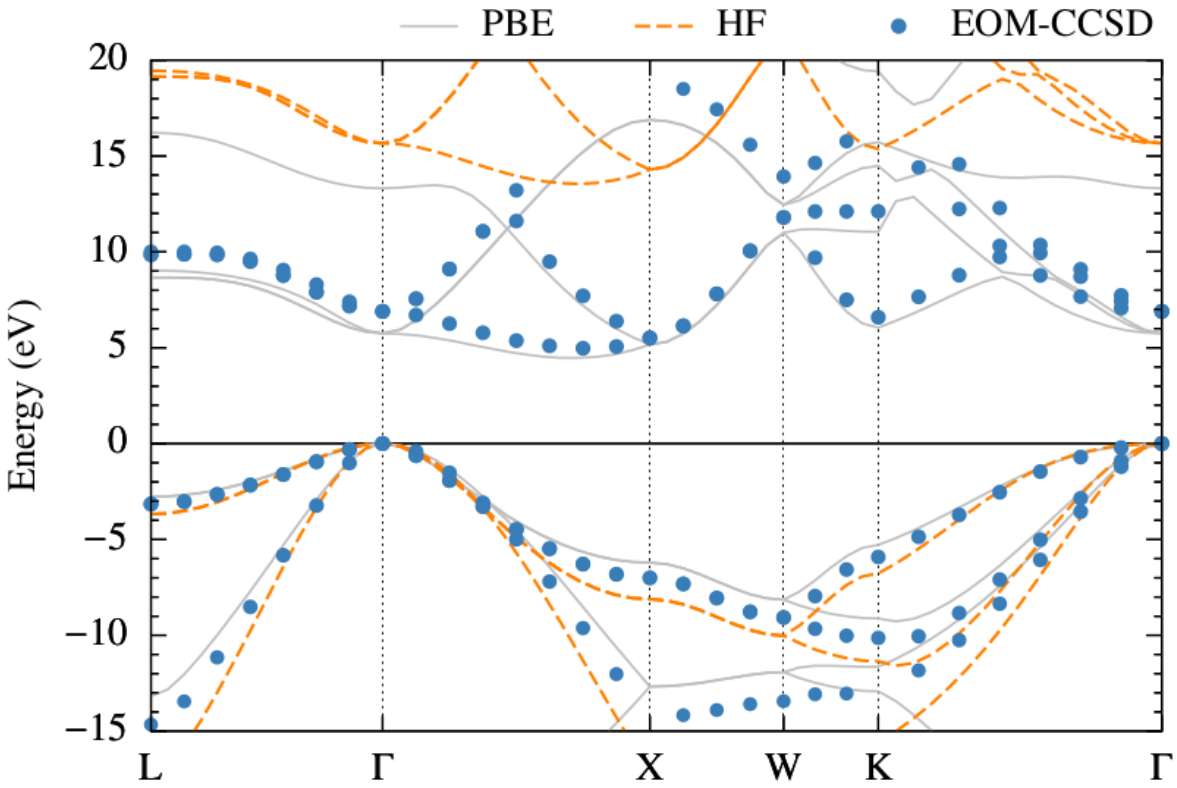


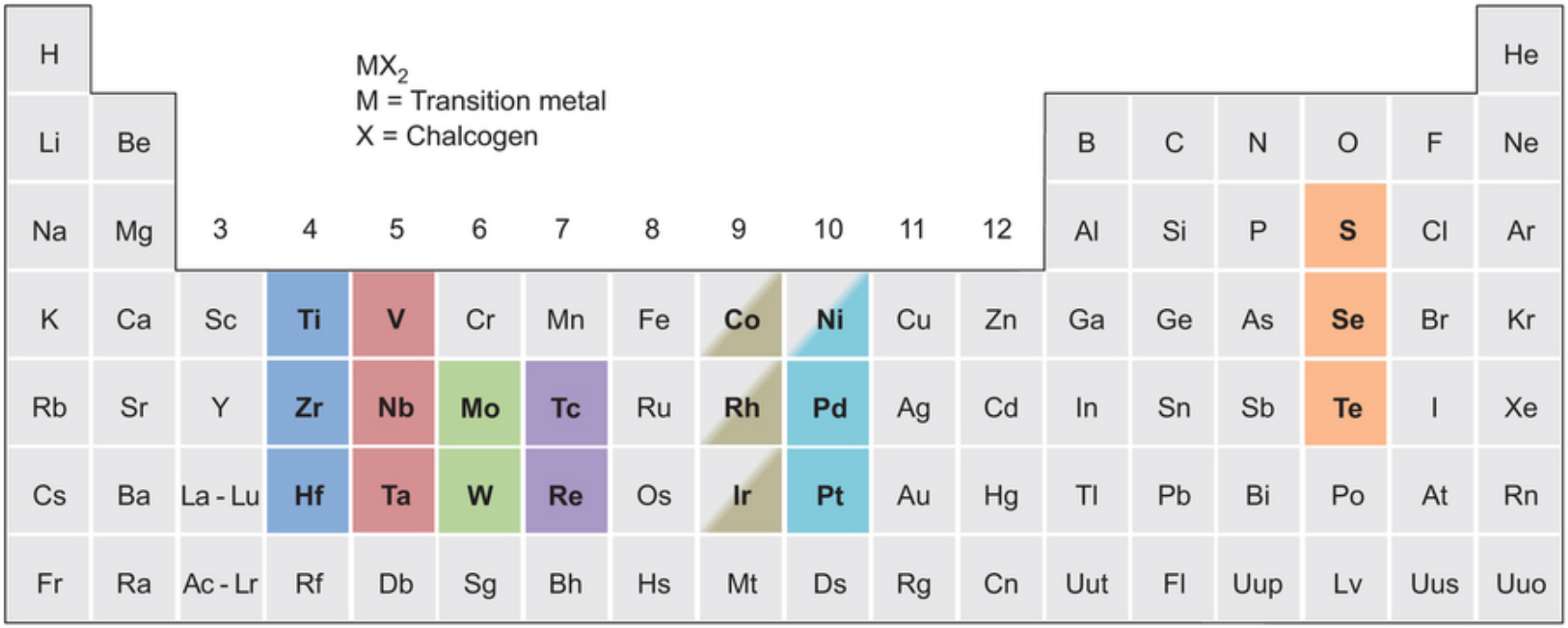
FIG. 4. Band structure of diamond calculated with DFT (PBE), HF, and EOM-CCSD, using the DZVP single-particle basis and a $3 \times 3 \times 3$ k-point mesh.

McClain et. al., Journal of chemical theory and computation 13(3) (2017)

2D materials

2D materials family

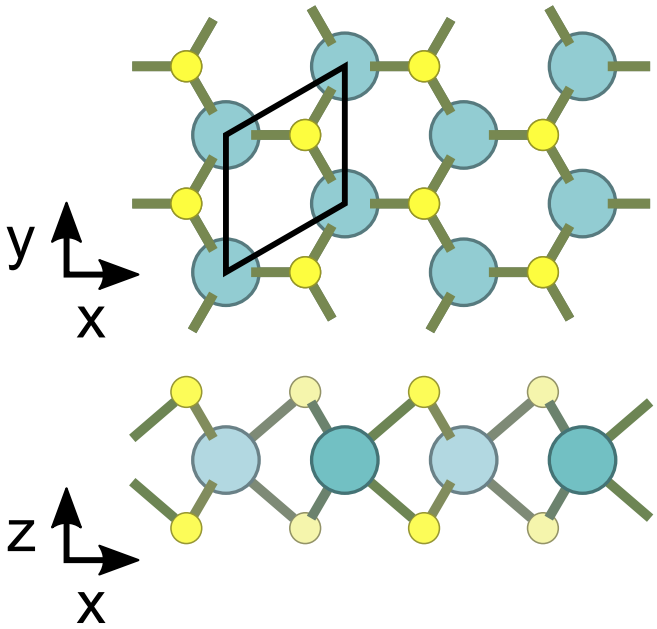
Graphene, graphane, fluorographene, chlorographene, silicene, germanene, silicane, fluorosilicene, fluorogermanene, chlorogermanene, BN, transition metal dichalcogenides MX_2 , M = transition metal, X = chalcogen: MoS_2, $ReSe_2$, ...

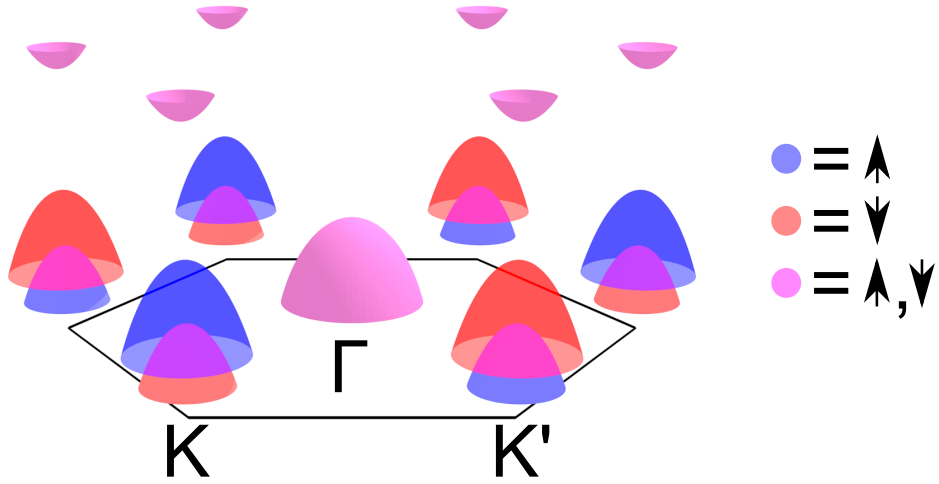


M. Chhowalla, et al., Nat Chem **5**, 263275 (2013)

MoS_2

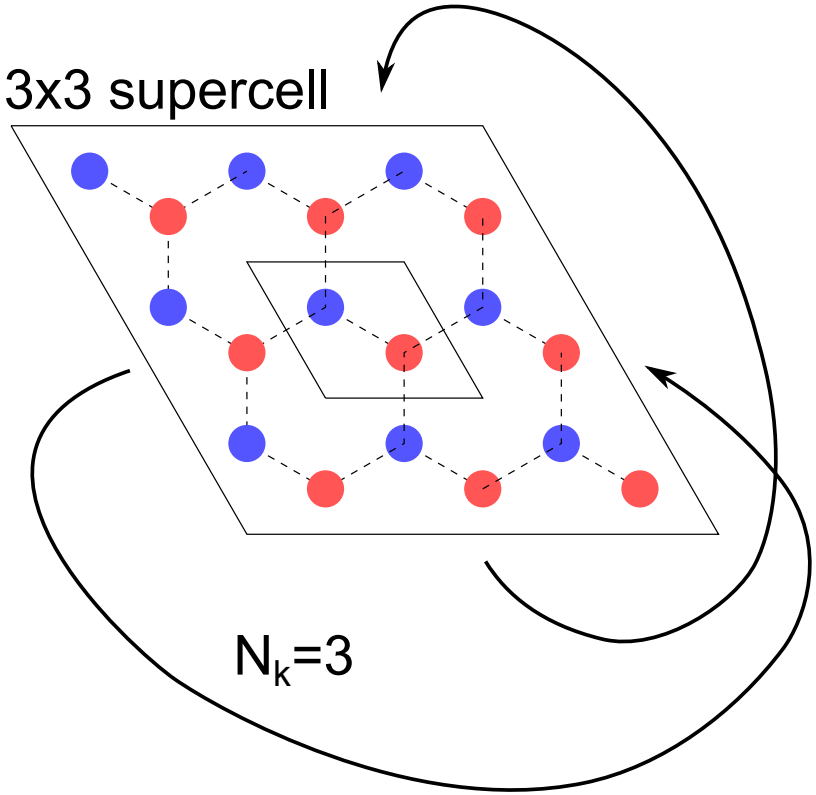
2H phase

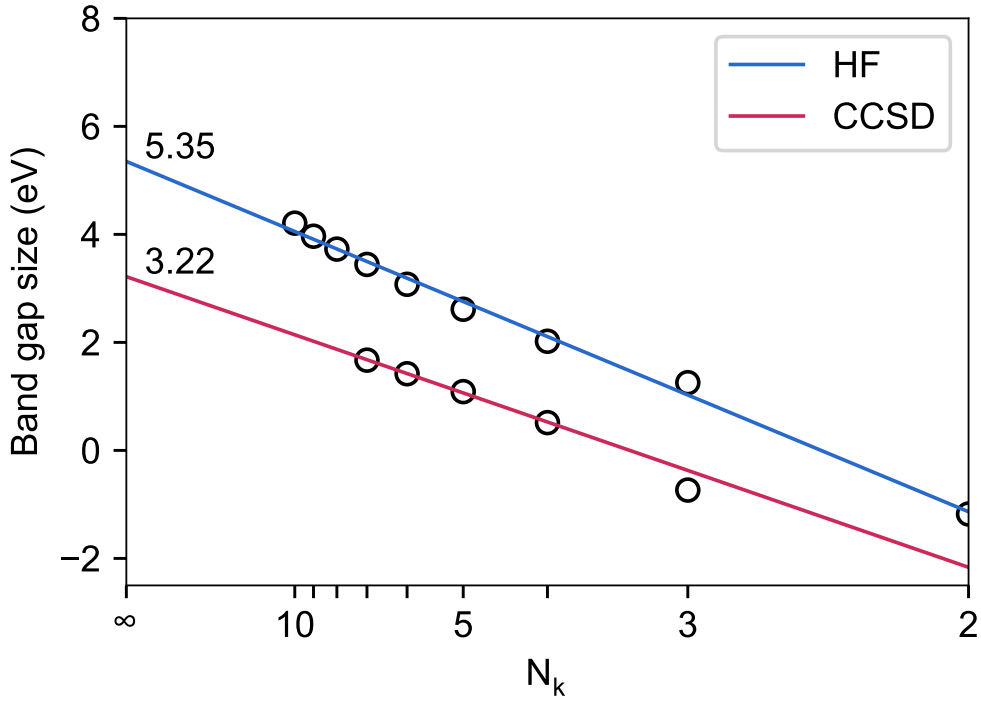




- hexagonal lattice, 3 atoms/unit cell
- semiconductor (direct band gap at K, K')
- spin-orbit effects
- exfoliated similarly to graphene

Setup



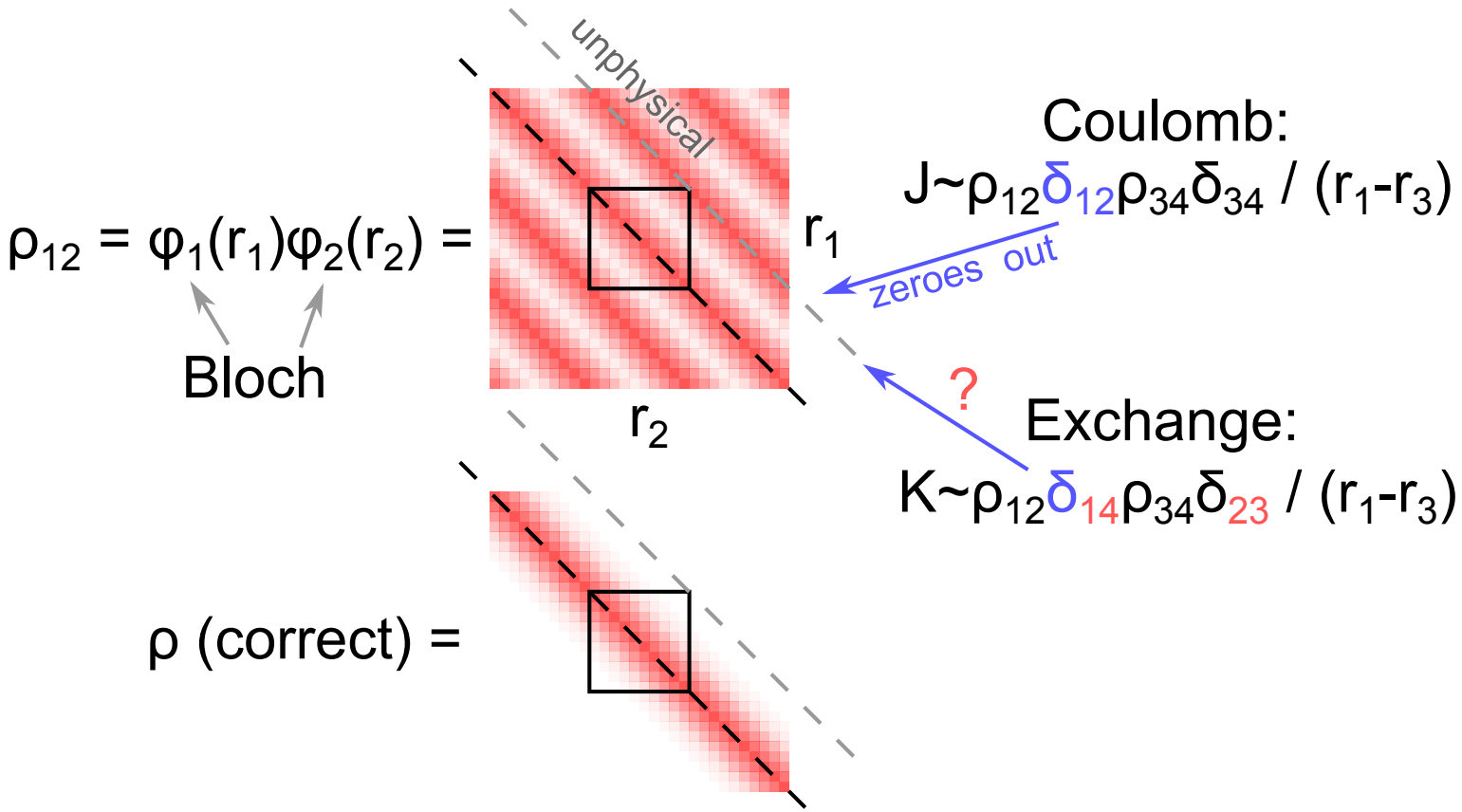


- gaussian Bloch orbitals, dzvp atomic basis set, spin-restricted theory;
- Brillouin zone sampling;
- ground-state CC + equation-of-motion IP and EA roots ($N_{\mathrm{elec}} - 1$, $N_{\mathrm{elec}} + 1$ spaces);
- $gap = \max E_{\mathrm{EA}} - \min E_{\mathrm{IP}}$

Extrapolation of the band gap

$$\Delta_g \sim \Delta_\infty - A/N_k$$

Source: error in 4-center integrals (also known as $G = 0$ problem or exchange divergence) caused by periodic boundary conditions:



3rd dimension

To model a 2D material ...

- with DFT $\rightarrow$ make L_z large enough;
- with exact exchange $\rightarrow$?

$$(pq|rs) \sim \sum_{G \neq 0} w \frac{1}{G^2}, \quad G = nb \quad n \in \mathbb{Z}$$

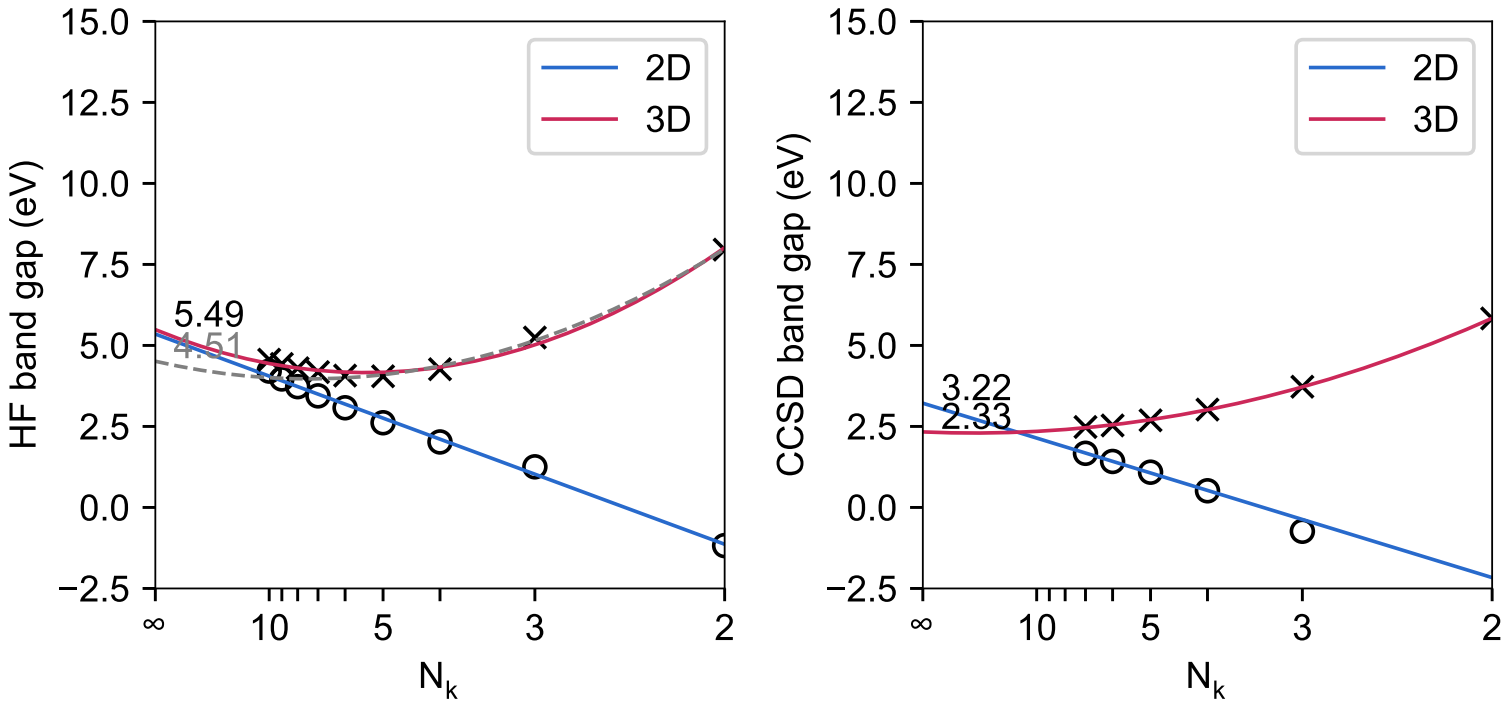
$$w = \frac{1}{V} = \frac{1}{S \cdot L_z}, \quad G_{\min} \sim \frac{1}{L_z}$$

$$(pq|rs) \sim \frac{L_z}{S} \text{ - diverges } L_z \rightarrow \infty,\ S = \text{const}$$

- either use analytic Fourier treatment along z: $(pq|rs) \sim \sum_{G \neq 0} w \frac{1}{G}$
- or use a uniform k-sampling $S \sim L_z^2$: $G_{\min} \sim \frac{1}{\sqrt{S}}$, error

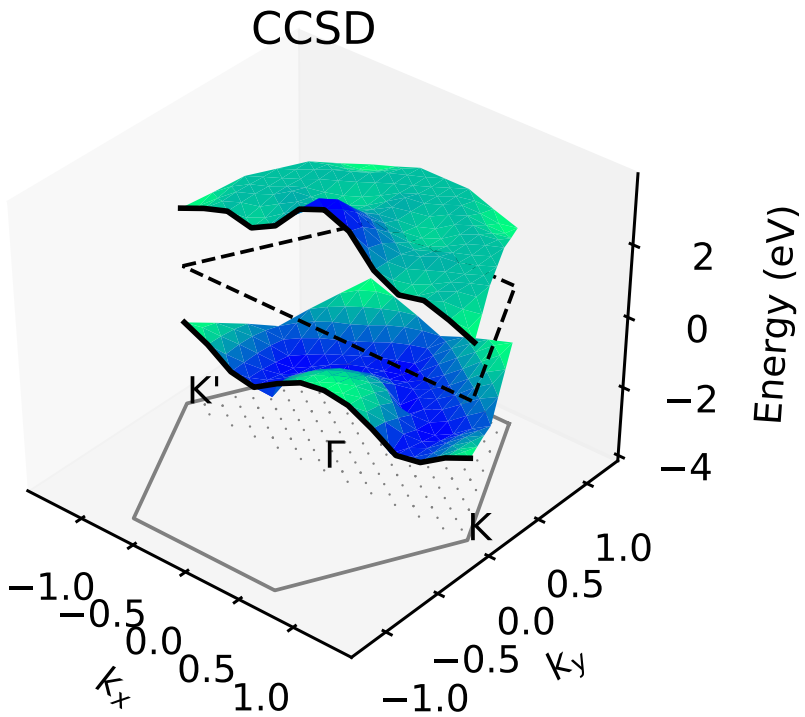
$$(pq|rs) \sim \frac{1}{\sqrt{S}}$$

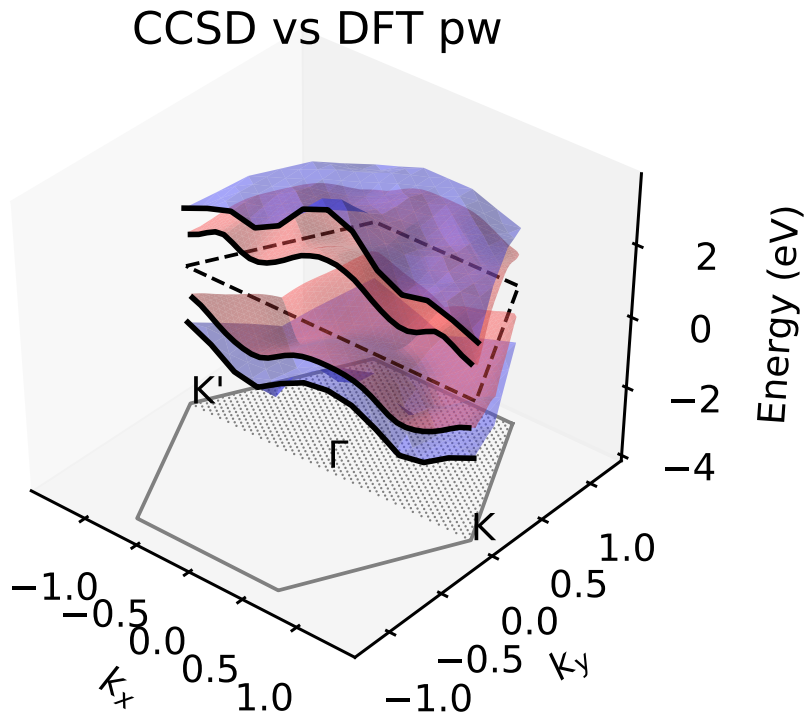
Infinite limit



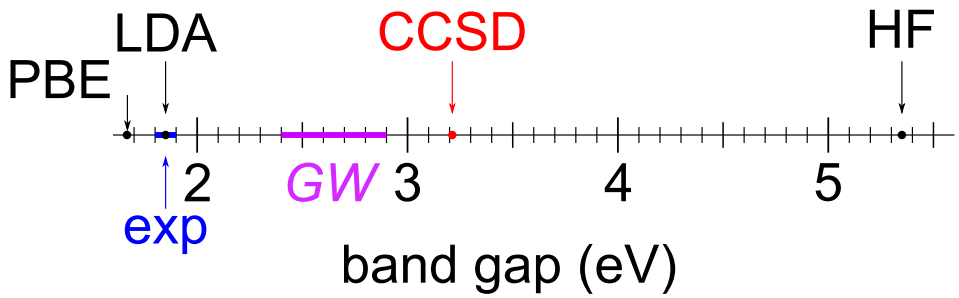
- 2D: $\Delta_g \sim \Delta_\infty + \mathrm{const}/N_k$
- 3D: $\Delta_g \sim \begin{cases} \Delta_\infty + \mathrm{const} \cdot L_z/N_k^2, & N_k \ll L_z \\ \Delta_\infty + \mathrm{const}/N_k, & N_k \sim L_z \\ \Delta_\infty + \mathrm{const}, & N_k \gg L_z \end{cases}$

Electronic band structure





Experiment vs theory



Possible reasons for the discrepancy:

1. Theory fails:
   - CCSD is not good enough;
   - slow convergence wrt basis set;
   - features of $O(g) \rightarrow$ too few k-points;
2. Model is wrong
   - substrate, defects and doping

Mak et. el., PRL **105** 136805 (2010)
Ramasubramaniam, PRB **86** 115409 (2012)
Qiu et. al., PRB **93** 235435 (2016)

Other 2D transition metal dichalcogenides

The size of the band gap in 2D TMDs (eV)

	MoS_2	$MoSe_2$	WS_2	WSe_2
PBE	1.7	1.5	1.7	1.3
GW	2.8 +1.1	2.4 +0.9	2.9 +1.2	2.4 +1.1
CCSD	3.2 +0.4	2.8 +0.4	3.4 +0.5	3.0 +0.6

Conclusions

- Ground and excited many-body states of a 2D crystal calculated;
- Qualitative agreement, quantitative differences in the electronic band structure of 2D materials;
- Systematic corrections of the band gap size across the family of materials;
- Open questions regarding the agreement with experiment

Thank you