Predictive Computing for Condensed Matter

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Monte Carlo MP

Very long $O(n^4)$ summation of products of two 6-dimensional integrals

$$E^{(2)} = \sum_{i,j}^{occ}\sum_{a,b}^{vir} \frac{\langle ab|ij\rangle\langle ij|ab\rangle}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

Explicit two-electron integrals

$$E^{(2)} = \sum_{i,j}^{occ}\sum_{a,b}^{vir} \frac{\int \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)\frac{1}{r_{12}}\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \int \varphi_i(\mathbf{r}_3)\varphi_j(\mathbf{r}_4)\frac{1}{r_{34}}\varphi_a(\mathbf{r}_3)\varphi_b(\mathbf{r}_4)d\mathbf{r}_3 d\mathbf{r}_4}{\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b}$$

Laplace transformation of the denominator

$$E^{(2)} = -\sum_{i,j}^{occ}\sum_{a,b}^{vir} \int \varphi_i(\mathbf{r}_1)\varphi_j(\mathbf{r}_2)\frac{1}{r_{12}}\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 \int \varphi_i(\mathbf{r}_3)\varphi_j(\mathbf{r}_4)\frac{1}{r_{34}}\varphi_a(\mathbf{r}_3)\varphi_b(\mathbf{r}_4)d\mathbf{r}_3 d\mathbf{r}_4 \int_0^\infty e^{(\varepsilon_i+\varepsilon_j-\varepsilon_a-\varepsilon_b)\tau}d\tau$$

Change of orders of summations and integrations

$$E^{(2)} = -\int\cdots\iint_0^\infty \frac{\sum_i^{occ}\varphi_i(\mathbf{r}_1)\varphi_i(\mathbf{r}_3)e^{\varepsilon_i\tau}\sum_j^{occ}\varphi_j(\mathbf{r}_2)\varphi_j(\mathbf{r}_4)e^{\varepsilon_j\tau}\sum_a^{vir}\varphi_a(\mathbf{r}_1)\varphi_a(\mathbf{r}_3)e^{-\varepsilon_a\tau}\sum_b^{vir}\varphi_b(\mathbf{r}_2)\varphi_b(\mathbf{r}_4)e^{-\varepsilon_b\tau}}{r_{12}r_{34}}d\mathbf{r}_1\cdots d\mathbf{r}_4 d\tau$$

Single 13-dimensional integral evaluated by Monte Carlo

$$E^{(2)} = -\int\cdots\iint_0^\infty \frac{G^-(\mathbf{r}_1,\mathbf{r}_3,\tau)G^-(\mathbf{r}_2,\mathbf{r}_4,\tau)G^+(\mathbf{r}_1,\mathbf{r}_3,\tau)G^+(\mathbf{r}_2,\mathbf{r}_4,\tau)}{r_{12}r_{34}}d\mathbf{r}_1\cdots d\mathbf{r}_4 d\tau$$

$$E = \int f(x)dx = \int \frac{f(x)}{g(x)}g(x)dx = \sum_{x \in g} \frac{f(x)}{g(x)}$$

weight function

Metropolis

Requirement 1: analytically integrable $\int g(x)dx = 1$

Requirement 2: cancellation of singularities $f(x)/g(x)$

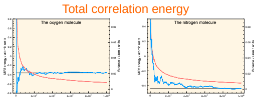
$$E^{(2)} = -\int\cdots\iint_0^\infty \frac{G^-(\mathbf{r}_1,\mathbf{r}_3,\tau)G^-(\mathbf{r}_2,\mathbf{r}_4,\tau)G^+(\mathbf{r}_1,\mathbf{r}_3,\tau)G^+(\mathbf{r}_2,\mathbf{r}_4,\tau)}{r_{12}r_{34}}d\mathbf{r}_1\cdots d\mathbf{r}_4 d\tau$$

Singularities

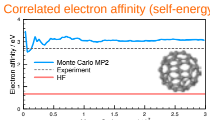
$$g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4) = \frac{1}{4E^2_{\text{Coulomb}}}\frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}}\frac{\rho(\mathbf{r}_3)\rho(\mathbf{r}_4)}{r_{34}}$$

$$\int g(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_4)d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 = 1$$

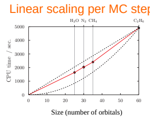
Total correlation energy



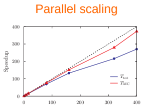
Correlated electron affinity (self-energy)



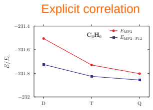
Linear scaling per MC step



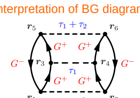
Parallel scaling



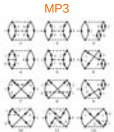
Explicit correlation



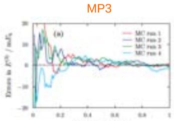
Real-space, imaginary-time Green's-function-trace interpretation of BG diagrams



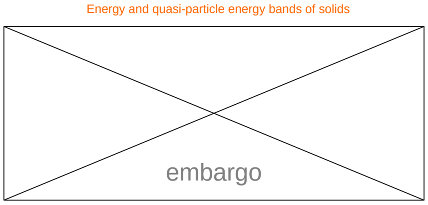
MP3



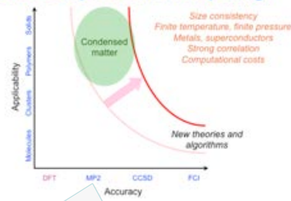
MP3



Energy and quasi-particle energy bands of solids



Frontiers of predictive computing



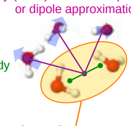
Applicability
Solids
Polymers
Clusters
Molecules
Condensed matter
Size consistency
Finite temperature, finite pressure
Metals, superconductors
Strong correlation
Computational costs
New theories and algorithms
DFT
MP2
CCSD
FCI
Accuracy

- The lowest-ranked member of a ***systematic*** series of converging approximations.
- Can describe covalent, ionic, hydrogen-bond, and ***dispersion*** interactions.
- ***Size consistent*** and applicable to solids.
- Accurate energy bands and ***band gaps***.
- The operation cost grows as $O(n^5)$, where n is the number of orbitals.
- The memory cost grows as $O(n^2)$ to $O(n^4)$.
- Parallelization is difficult.

Molecular Crystals

n-body ($n > 2$) Coulomb in point-charge or dipole approximation

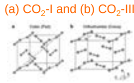
1 and 2-body Coulomb Exchange Correlation



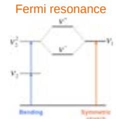
Pair energy in the presence of self-consistent atomic charges or dipoles

$$E = \sum_{i=1}^{n} E_i' + \sum_{i<j}^{n}\left(E_{ij}' - E_i' - E_j'\right) + \ldots$$

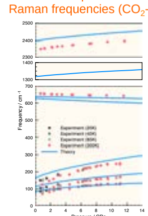
(a) CO_2-I and (b) CO_2-III



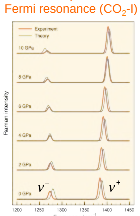
Fermi resonance



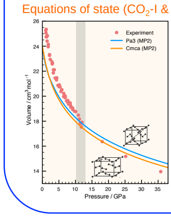
Pressure dependence of Raman frequencies (CO_2-I)



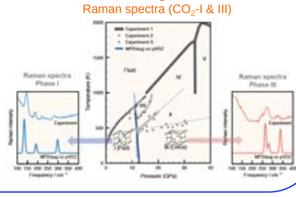
Pressure dependence of Fermi resonance (CO_2-I)



Equations of state (CO_2-I & III)



Phase diagram and Raman spectra (CO_2-I & III)



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[2] S. Hirata and X. He, *J. Chem. Phys.* **138**, 204112 (2013), "On the Kohn–Luttinger conundrum."
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[7] S. Y. Willow and S. Hirata, *J. Chem. Phys.* **140**, 024111 (2014), "Stochastic, real-space, imaginary-time evaluation of third-order Feynman–Goldstone diagrams."
[8] X. He, S. Ryu, and S. Hirata, *J. Chem. Phys.* **140**, 024702 (2014), "Finite-temperature second-order many-body perturbation and Hartree-Fock theories for one-dimensional solids: An application to Peierls and charge-density-wave transitions in conjugated polymers."
[9] S. Hirata, K. Gilliard, X. He, J. Li, and O. Sode, *Acc. Chem. Res.* (ASAP online, 2014), "Ab initio molecular crystal structures, spectra, and phase diagrams."
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Finite-temperature MP, CC, CI

Zero temperature

$$E^{(2)}_{\text{MP}} = \frac{1}{4}\sum_{i,j}^{\text{occupied}}\sum_{a,b}^{\text{virtual}}\sum_{\mathbf{k}_i,\mathbf{k}_j,\mathbf{k}_a} \frac{v^{a\mathbf{k}_a b\mathbf{k}_b}_{i\mathbf{k}_i j\mathbf{k}_j} v^{i\mathbf{k}_i j\mathbf{k}_j}_{a\mathbf{k}_a b\mathbf{k}_b}}{\varepsilon_{i\mathbf{k}_i}+\varepsilon_{j\mathbf{k}_j}-\varepsilon_{a\mathbf{k}_a}-\varepsilon_{b\mathbf{k}_b}}$$

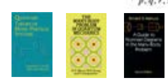
Finite temperature

$$E^{(2)}_{\text{MP}} = \frac{1}{4}\sum_{p,q,r,s}^{\text{all}}\sum_{\mathbf{k}_p,\mathbf{k}_q,\mathbf{k}_r} \frac{v^{r\mathbf{k}_r s\mathbf{k}_s}_{p\mathbf{k}_p q\mathbf{k}_q} v^{p\mathbf{k}_p q\mathbf{k}_q}_{r\mathbf{k}_r s\mathbf{k}_s} f^-_{p\mathbf{k}_p} f^-_{q\mathbf{k}_q} f^+_{r\mathbf{k}_r} f^+_{s\mathbf{k}_s}}{\varepsilon_{p\mathbf{k}_p}+\varepsilon_{q\mathbf{k}_q}-\varepsilon_{r\mathbf{k}_r}-\varepsilon_{s\mathbf{k}_s}}$$

Fermi-Dirac vacancy

Fermi-Dirac occupancy

$$\frac{1}{e^{\beta(\varepsilon_{p\mathbf{k}_p}-\varepsilon_F)}+1}$$



> March *et al.*, "The Many-Body Problem in Quantum Mechanics"
> "..., a note of caution is called for whenever we attempt to calculate zero-temperature properties from an expression for the same quantities at non-zero temperatures T by taking the limit T tends to 0. The physics is not the same in both cases."

> Kohn and Luttinger, *Phys. Rev.* (1960)
> "The BG (Brueckner–Goldstone perturbation) series is therefore in general not correct."

Conventional

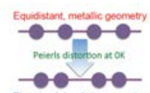
$$E^{(2)}_{\text{MP}} = \frac{1}{4}\sum_{p,q,r,s}^{\text{all}}\sum_{\mathbf{k}_p,\mathbf{k}_q,\mathbf{k}_r} \frac{v^{r\mathbf{k}_r s\mathbf{k}_s}_{p\mathbf{k}_p q\mathbf{k}_q} v^{p\mathbf{k}_p q\mathbf{k}_q}_{r\mathbf{k}_r s\mathbf{k}_s} f^-_{p\mathbf{k}_p} f^-_{q\mathbf{k}_q} f^+_{r\mathbf{k}_r} f^+_{s\mathbf{k}_s}}{\varepsilon_{p\mathbf{k}_p}+\varepsilon_{q\mathbf{k}_q}-\varepsilon_{r\mathbf{k}_r}-\varepsilon_{s\mathbf{k}_s}}$$

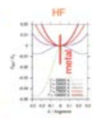
Renormalized (new!)

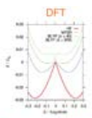
$$E^{(2)}_{\text{MP}} = \frac{1}{4}\sum_{p,q,r,s}^{\text{all}}\sum_{\mathbf{k}_p,\mathbf{k}_q,\mathbf{k}_r} \frac{v^{r\mathbf{k}_r s\mathbf{k}_s}_{p\mathbf{k}_p q\mathbf{k}_q} v^{p\mathbf{k}_p q\mathbf{k}_q}_{r\mathbf{k}_r s\mathbf{k}_s} f^-_{p\mathbf{k}_p} f^-_{q\mathbf{k}_q} f^+_{r\mathbf{k}_r} f^+_{s\mathbf{k}_s}}{f^-_{p\mathbf{k}_p}\varepsilon_{p\mathbf{k}_p}+f^-_{q\mathbf{k}_q}\varepsilon_{q\mathbf{k}_q}-f^+_{r\mathbf{k}_r}\varepsilon_{r\mathbf{k}_r}-f^+_{s\mathbf{k}_s}\varepsilon_{s\mathbf{k}_s}}$$

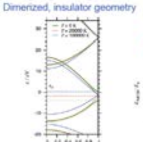
Thermal Wick's theorem: Matsubara 1955; Thouless 1957; Mukherjee 1993-1997; Kutzelnigg & Mukherjee 1997; Kong, Nooijen, & Mukherjee 2010

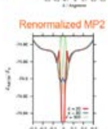
Theory	Divergence in metals	Anomalous diagrams at 0K
Zero-temperature MP2	$\lim_{\delta\to 0}(-\log\delta)$	Zero
Conventional finite-temperature MP2	$\lim_{\delta\to 0}\delta^{-1}$	Non-zero
Renormalized finite-temperature MP2	$\lim_{\delta\to 0}(-\log\delta)$	Zero

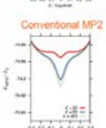


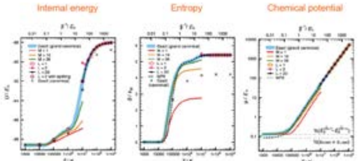












Finite-temperature FCI