

Observables at zero and at finite temperature

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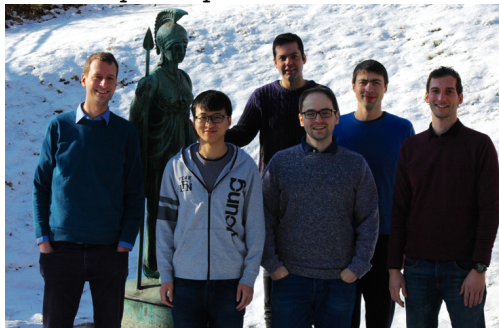


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acknowledgements

- computational quantum chemistry at TU wien

<http://cqc.tuwien.ac.at/>

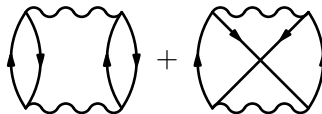


Andreas Grüneis, Ke Liao, Theodoros Tsatsoulis, Alejandro Gallo, Thomas Gruber, FH and Andreas Irmeler (new member)

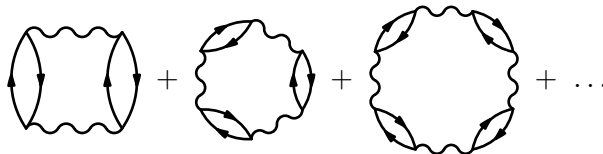
- coupled cluster code for periodic systems cc4s, release 2018
- CCSD(T) for ≈ 40 atoms, interface to VASP

metals

- interesting reaction on metal surfaces
- band gap $\propto 1/\text{system size}$
- finite order PT diverges



- resummed PT works with single reference: RPA, CC for UEG

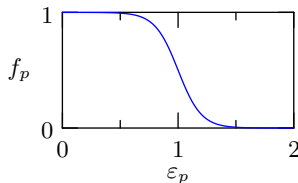


- degenerate reference for finite N metallic systems

finite temperature approach

- DFT: partially occupy levels ε_p degenerate within $\varepsilon_F \pm \delta$
- SCF cycle unstable for too small degeneracy window δ
- Fermi–Dirac with artificial temperature β^{-1} & Fermi level μ

$$f_p = \frac{e^{-\beta(\varepsilon_p - \mu)}}{1 + e^{-\beta(\varepsilon_p - \mu)}}$$



- reasonable for density, what about wavefunction?
- costly MBPT at $T > 0$ in Matsubara frequencies ω_n
- efficient finite order MBPT in imaginary time τ on $[0, \beta]$

can imaginary time MBPT be resummed?

background

finite temperature

- self consistent field

- many body perturbation theory

- expectation values

imaginary time resummation

summary

$$T > 0$$

- metals: surface reactions
- graphene
- aromatics
- plasma: emission spectra
- hydrogen phases: Peierls transition
Hermes *et al.*, JCP **143**, 102818 (2015).
- ion or e^- sources: work function
- nuclear matter



grand canonical ensemble

- energy & electrons exchanged with bath
- grand canonical ensemble at fixed μVT
- constraints on entropy max.: Lagrangian multipliers β, μ
- e.g. single level, energy ε , occupation $n \in 0, 1$

$$\hat{\rho} = e^{-\beta(\varepsilon - \mu)\hat{c}^\dagger \hat{c}}$$

- probability of finding state $|n = 0, 1\rangle \propto \text{Tr}\{\hat{\rho} |n\rangle\langle n|\}$

$$P(|1\rangle) = \frac{e^{-\beta(\varepsilon - \mu)}}{1 + e^{-\beta(\varepsilon - \mu)}}$$

- denominator $\sum_n \text{Tr}\{\hat{\rho} |n\rangle\langle n|\} = \mathcal{Z}(\beta, \mu)$: partition function

independent particles at $T > 0$

- separate systems for each level p , energy ε_p , occupation n_p :

$$\hat{\rho}_0 = \bigotimes_p e^{-\beta(\varepsilon_p - \mu)\hat{c}_p^\dagger \hat{c}_p} = e^{-\beta \sum_p (\varepsilon_p - \mu)\hat{c}_p^\dagger \hat{c}_p} = e^{-\beta(\hat{H}_0 - \mu\hat{N})}$$

- partition function

$$\mathcal{Z}_0(\beta, \mu) = \sum_{n_1, n_2, \dots} \text{Tr}\{\hat{\rho}_0 |n_1 n_2 \dots\rangle \langle n_1 n_2 \dots|\} = \prod_p (1 + e^{-\beta(\varepsilon_p - \mu)})$$

- e.g. probability of finding state $|100 \dots\rangle$:

$$P(|100 \dots\rangle) = \underbrace{\frac{e^{-\beta(\varepsilon_1 - \mu)}}{1 + e^{-\beta(\varepsilon_1 - \mu)}}}_{=: f_1} \underbrace{\frac{1}{1 + e^{-\beta(\varepsilon_2 - \mu)}}}_{=: f^2} \dots =: f_1^{2,3,\dots}$$

Wick's theorem at $T > 0$

- HF/MBPT require contractions $\overbrace{\hat{c}_q \hat{c}_p^\dagger} = \hat{c}_q \hat{c}_p^\dagger - N^{T>0}[\hat{c}_q \hat{c}_p^\dagger]$
Matsubara, Prog. Theor. Phys. **4**, 351–378 (1955).
- define new operators \hat{a}, \hat{b}

$$\begin{aligned}\hat{c}_p^\dagger &= (1 - g_p)\hat{a}_p^\dagger + g_p\hat{b}_p & \text{with } \hat{c}_p^\dagger &= \hat{a}_p^\dagger = \hat{b}_p \\ \hat{c}_p &= (1 - g_p)\hat{a}_p + g_p\hat{b}_p^\dagger & \hat{c}_p &= \hat{a}_p = \hat{b}_p^\dagger\end{aligned}$$

with scalar g_p for each level (no canonical transformation)

- define normal ordering $N^{T>0}[\dots]$: \hat{a}^\dagger then \hat{b}^\dagger then \hat{b} then \hat{a}

$$\text{e.g. } N^{T>0}[\hat{b}^\dagger \hat{b} \hat{a} \hat{a}^\dagger] = -\hat{a}^\dagger \hat{b}^\dagger \hat{b} \hat{a}$$

- choose g_p s.t. expectation values of normal ordered $\hat{c} \dots$ vanish

$$\sum_{n_1 \dots} \text{Tr}\{\hat{\rho}_0 N^{T>0}[\hat{c}_p^\dagger \hat{c}_q] |n_1 \dots\rangle \langle n_1 \dots|\} = 0 \quad \Leftrightarrow \quad g_p^2 = f_p \quad \forall p$$

- contractions in $\hat{\rho}_0$ VEVs: $\langle \overbrace{\hat{c}_j^\dagger \hat{c}_i} \rangle_0 = \delta_j^i f_i, \quad \langle \overbrace{\hat{c}_a \hat{c}_b^\dagger} \rangle_0 = \delta_a^b f^a$

Hartree–Fock at $T > 0$

0. start with reasonable ψ_p, ε_p
1. choose either $\langle \hat{N} \rangle_0$ or μ , determine the other
2. mean field: contract \hat{H} to single electron
convention: sum indices occurring only on rhs

$$F_q^p = h_q^p + f_j (V_{qj}^{pj} - V_{qj}^{jp}) \quad \text{with} \quad f_j = \frac{e^{-\beta(\varepsilon_j - \mu)}}{1 + e^{-\beta(\varepsilon_j - \mu)}}$$

$$= h_q^p + \text{diagram 1} + \text{diagram 2}$$

3. solve F_q^p for eigensystem ψ_p, ε_p
4. if not converged repeat from 1.
5. minimized free energy:

$$F^{\text{HF}} = -\frac{1}{\beta} \log \mathcal{Z}_0(\beta, \mu) + \mu \langle \hat{N} \rangle_0 - \underbrace{f_i f_j (V_{ij}^{ij} - V_{ij}^{ji})}_{1^{\text{st}} \text{ order } \hat{V}_{\text{eff}}} + \underbrace{\frac{1}{2} f_i f_j (V_{ij}^{ij} - V_{ij}^{ji})}_{1^{\text{st}} \text{ order } \hat{V}}$$

many body perturbation theory at $T > 0$

- split into reference and correlation part (Zassenhaus formula)

$$\hat{\rho} = e^{-\beta(\hat{H}_0 + \hat{H}_1 - \mu\hat{N})} = \underbrace{e^{-\beta(\hat{H}_0 - \mu\hat{N})}}_{\hat{\rho}_0} \underbrace{e^{-\beta\hat{H}_1} e^{+\beta^2/2[\hat{H}_0, \hat{H}_1]} \dots}_{\hat{S}}$$

- insert into Bloch equation $-\partial\hat{\rho}/\partial\beta = (\hat{H} - \mu\hat{N})\hat{\rho}$:

$$-\frac{\partial(\hat{\rho}_0\hat{S})}{\partial\beta} = (\hat{H}_0 - \mu\hat{N})\hat{\rho}_0\hat{S} - \hat{\rho}_0\frac{\partial\hat{S}}{\partial\beta} = (\hat{H}_0 + \hat{H}_1 - \mu\hat{N})\hat{\rho}_0\hat{S}$$

- Bloch equation for correlation part

$$-\frac{\partial\hat{S}(\beta, \mu)}{\partial\beta} = \underbrace{e^{+\beta(\hat{H}_0 - \mu\hat{N})} \hat{H}_1 e^{-\beta(\hat{H}_0 - \mu\hat{N})}}_{\hat{H}_1(\beta, \mu)} \hat{S}(\beta, \mu)$$

- interaction picture analogue

linked cluster theorem at $T > 0$

- integrate Bloch equation and iterate

$$\hat{S}(\beta, \mu) = \sum_{n=0}^{\infty} (-1)^n \int_{0 < \tau_1 < \dots < \tau_n < \beta} d\tau_1 \dots d\tau_n \hat{H}_1(\tau_n) \dots \hat{H}_1(\tau_1)$$

- correlation partition function

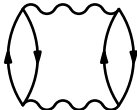
$$\frac{\mathcal{Z}(\beta, \mu)}{\mathcal{Z}_0(\beta, \mu)} = \frac{\sum_{n_1 \dots} \text{Tr}\{\hat{\rho}_0 \hat{S}(\beta, \mu) |n_1 \dots\rangle \langle n_1 \dots|\}}{\sum_{n_1 \dots} \text{Tr}\{\hat{\rho}_0 |n_1 \dots\rangle \langle n_1 \dots|\}} = \langle \hat{S}(\beta, \mu) \rangle_0$$

- all $\langle \cdot \rangle_0 = \exp(\langle \cdot \rangle_0')$ of **connected** terms, starting with $n = 1$

$$\begin{aligned} & \log \mathcal{Z}(\beta, \mu) - \log \mathcal{Z}_0(\beta, \mu) \\ &= \sum_{n=1}^{\infty} (-1)^n \int_{0 < \tau_1 < \dots < \tau_n < \beta} d\tau_1 \dots d\tau_n \langle \hat{H}_1(\tau_n) \dots \hat{H}_1(\tau_1) \rangle_0' \end{aligned}$$

example: correlation free energy in MP2

- only direct and exchange term remain $\log \mathcal{Z}^{(2)}(\beta, \mu)$

$$\begin{aligned}
 &= \sum_{n=2}^2 (-1)^n \int_{0 < \tau_1 < \dots < \tau_n < \beta} d\tau_1 \dots d\tau_n \langle \hat{H}_1(\tau_n) \dots \hat{H}_1(\tau_1) \rangle'_0 \\
 &= \int_0^\beta d\tau_1 \int_{\tau_1}^\beta d\tau_2 e^{-(\tau_2 - \tau_1) \Delta_{ij}^{ab}} \frac{1}{4} \langle \overbrace{V_{ab}^{ij} \hat{c}_i^\dagger \hat{c}_j^\dagger \hat{c}_b \hat{c}_a V_{ij}^{ab} \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_j \hat{c}_i} + \dots \rangle_0 \\
 &= \frac{e^{-\beta \Delta_{ij}^{ab}} + \beta \Delta_{ij}^{ab} - 1}{\Delta_{ij}^{2ab}} \frac{1}{2} f_{ij}^{ab} (V_{ab}^{ij} - V_{ab}^{ji}) V_{ij}^{ab}
 \end{aligned}$$


with $\Delta_{ij}^{ab} = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$

- $F^{\text{MP2}} = -\frac{1}{\beta} \log \mathcal{Z}^{(2)}(\beta, \mu) + F^{\text{HF}}$
- careful: correlation also affects $\langle \hat{N} \rangle$ (-0.0002 in H_2 at 1 eV)

expectation values

- conjugate to fixed quantities β & μ :

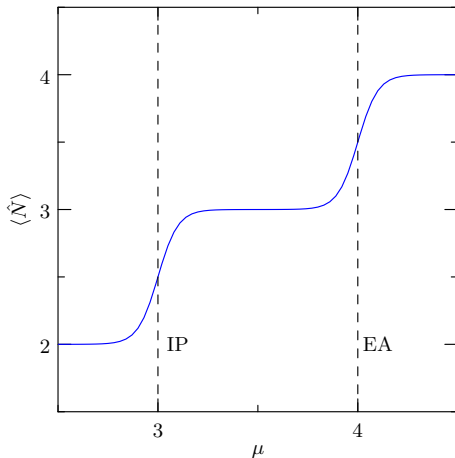
$$\begin{aligned}\langle \hat{H} \rangle &= \frac{\partial}{-\partial \beta} \log \mathcal{Z}(\beta, \mu) & \langle \hat{N} \rangle &= \frac{\partial}{\beta \partial \mu} \log \mathcal{Z}(\beta, \mu) \\ \langle \Delta^2 \hat{H} \rangle &= \frac{\partial^2}{(-\partial \beta)^2} \log \mathcal{Z}(\beta, \mu) & \langle \Delta^2 \hat{N} \rangle &= \frac{\partial^2}{(\beta \partial \mu)^2} \log \mathcal{Z}(\beta, \mu) \\ \vdots & & \vdots & \end{aligned}$$

with $\Delta \hat{A} = \hat{A} - \langle \hat{A} \rangle$

- linearity and size extensivity inherited from $\log \mathcal{Z}$
- statistical moments of spectrum of *interacting* Hamiltonian



example: work function

- work function: $\langle \hat{N} \rangle$ as function of μ



- $T > 0$ analogue to IP/EA

imaginary time many body perturbation theory

	τ integration	$\langle \hat{c}_a \hat{c}_b^\dagger \rangle_0$	diagrams
$T = 0$	$\int_{-\infty < \tau_1 < \dots < \tau_{n-1} < \tau_n = 0} d\tau_1 \dots d\tau_{n-1}$	δ_a^b	
$T > 0$	$\frac{1}{\beta} \int_{0 < \tau_1 < \dots < \tau_n < \beta} d\tau_1 \dots d\tau_n$	$\delta_a^b f^a$	

- MP2 at $T = 0$ in imaginary time MBPT:

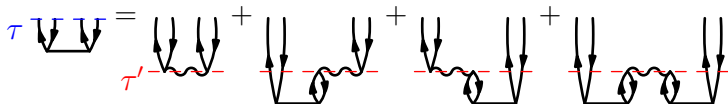
$$E_c = (-1) \int_{-\infty}^0 d\tau_1 e^{-(0-\tau_1)\Delta_{ij}^{ab}} \frac{1}{2} (V_{ab}^{ij} - V_{ab}^{ji}) V_{ij}^{ab}$$

- MP2 at $T > 0$:

$$F_c = -\frac{1}{\beta} \iint_{0 < \tau_1 < \tau_2 < \beta} d\tau_1 d\tau_2 e^{-(\tau_2-\tau_1)\Delta_{ij}^{ab}} \frac{1}{2} f_{ij}^{ab} (V_{ab}^{ij} - V_{ab}^{ji}) V_{ij}^{ab}$$

resummation as recursive recipe at $T = 0$

- given: doubles amplitudes T_{ij}^{ab} at τ' of all possible rings
- concatenate \hat{H}_1 at τ' with T_{ij}^{ab} & propagate to later $\tau > \tau'$
- yields amplitudes T_{ij}^{ab} at τ of all possible rings: Dyson-like eq.



$$T_{ij}^{ab}(\tau) = (-1) \int_{-\infty < \tau' < \tau} d\tau' e^{-(\tau - \tau')\Delta_{ij}^{ab}} \left(V_{ij}^{ab} + V_{id}^{al} T_{lj}^{db}(\tau') + V_{kj}^{cb} T_{ik}^{ac}(\tau') + V_{cd}^{kl} T_{ik}^{ac}(\tau') T_{lj}^{db}(\tau') \right)$$

- infinite time to relax, steady state: $T_{ij}^{ab}(\tau) = T_{ij}^{ab}(\tau') = T_{ij}^{ab}$
- set $\tau = 0$ & integrate τ' gives drCCD amplitudes equations

recursive recipe at $T > 0$

- use thermal contractions $\langle \hat{c}_a \hat{c}_b^\dagger \rangle_0 = f^a \delta_a^b$
- finite time β to relax: no steady state

$$R_{ij}^{ab}(\tau') = V_{ij}^{ab} + \dots + f_{kl}^{cd} V_{cd}^{kl} T_{ik}^{ac}(\tau') T_{lj}^{db}(\tau') \quad (1)$$

$$T_{ij}^{ab}(\tau) = \int_0^\tau d\tau' e^{-(\tau-\tau')\Delta_{ij}^{ab}} R_{ij}^{ab}(\tau')$$

$$\xrightarrow{\mathcal{L}} \tilde{T}_{ij}^{ab}(s) = \frac{1}{s + \Delta_{ij}^{ab}} \tilde{R}_{ij}^{ab}(s) \quad (2)$$

solve with numerical Laplace transformation on grid (τ_n) , (s_m) :

$$\begin{array}{ccc} T(\tau_n) & \xrightarrow{(1)} & R(\tau_n) \\ \mathcal{L}^{-1} \uparrow & & \downarrow \mathcal{L} \\ \tilde{T}(s_m) & \xleftarrow{(2)} & \tilde{R}(s_m) \end{array}$$

retrieving $\log \mathcal{Z}$

- perturbation expansion:

	τ integration	$\langle \overline{\hat{c}_a} \hat{c}_b^\dagger \rangle_0$
$T > 0$	$\int_{0 < \tau_1 < \dots < \tau_n < \beta} d\tau_1 \dots d\tau_n$	$\delta_a^b f^a$

contract amplitudes with $\hat{H}_1(\tau)$ at all $\tau \in [0, \beta]$:

$$\begin{aligned}
 \log \mathcal{Z}^{\text{CC}} - \log \mathcal{Z}^{\text{HF}} &= \int_0^\beta d\tau f_{ij}^{ab} (V_{ab}^{ij} - V_{ab}^{ji}) T_{ij}^{ab}(\tau) \\
 &= \text{[Diagram 1]} + \text{[Diagram 2]}
 \end{aligned}$$

The diagrams show two terms in the perturbation expansion. The first term is a loop diagram with two vertices connected by two horizontal lines (top and bottom) and two vertical lines (left and right). The top horizontal line is dashed, and the bottom horizontal line is dashed. The left vertical line is dashed, and the right vertical line is dashed. The top horizontal line is labeled β and the bottom horizontal line is labeled 0 . The left vertical line is labeled τ and the right vertical line is labeled τ . The second term is a similar loop diagram, but with a cross inside the loop, indicating a different contraction.

retrieving derivatives of $\log \mathcal{Z}$

- correlation $\log \mathcal{Z}(\beta, \mu)$:

$$\log \mathcal{Z}^{\text{CC}} - \log \mathcal{Z}^{\text{HF}} = \int_0^\beta d\tau f_{ij}^{ab} (V_{ab}^{ij} - V_{ab}^{ji}) T_{ij}^{ab}(\tau)$$

- $\partial/(-\partial\beta)$: system of amplitude equations $T^{(1)}, R^{(1)}$

$$\begin{aligned} R^{(1)ab}_{ij}(\tau') &= \dots + f^{(1)cd}_{kl} V^{kl}_{cd} T^{(0)ac}_{ik}(\tau') T^{(0)db}_{lj}(\tau') \\ &\quad + \dots + f^{(0)cd}_{kl} V^{kl}_{cd} T^{(1)ac}_{ik}(\tau') T^{(0)db}_{lj}(\tau') \\ &\quad + \dots + f^{(0)cd}_{kl} V^{kl}_{cd} T^{(0)ac}_{ik}(\tau') T^{(1)db}_{lj}(\tau') \\ \tilde{T}^{(1)ab}_{ij}(s) &= \frac{1}{s + \Delta^{ab}_{ij}} \tilde{R}^{(1)ab}_{ij}(s) \end{aligned}$$

- derivatives of Fermi weights w.r.t. $(-\partial\beta)$:

$$f_p^{(1)} = +\varepsilon_p f_p^{(0)} f^{(0)p} \qquad f^{(1)p} = -\varepsilon_p f_p^{(0)} f^{(0)p}$$

numerical Laplace transform

- imaginary time&frequency grid minimizing max error $\forall I = \overset{a}{i}\overset{b}{j}$
- minimax algorithm fitting ≈ 12 points for error $< 10^{-5}$
- optimize forward & inverse Laplace transform matrix L_m^n & IL_n^m

$$f_I \frac{1}{s + \Delta_I} \approx f_I \sum_n L_m^n e^{-(\eta + i\nu_m)\tau_n} e^{-\Delta_I \tau_n} \quad \forall I \forall m$$

$$f_I e^{-\Delta_I \tau_n} \approx \frac{f_I}{2\pi} \sum_m IL_n^m e^{+(\eta + i\nu_m)\tau_n} \frac{1}{\eta + i\nu_m + \Delta_I} \quad \forall I \forall n$$

- condition number of LT can reach 10^{18} (!)
- use quadruple precision arithmetic for all optimizations
- optimize both direction L_m^n and IL_n^m separately

summary: finite order

- analytic imaginary time τ integration on $[0, \beta]$:

$$F^{\text{MP2}} - F^{\text{HF}} = - \frac{f_{ij}^{ab} - f_{ab}^{ij}}{4\Delta_{ij}^{ab}} (V_{ab}^{ij} - V_{ab}^{ji}) V_{ij}^{ab}$$

- complexity of MP2:

$$\mathcal{O}(N_o^2 N_v^2 N_F) \text{ for } \beta^{-1} \approx \mu - \varepsilon_1, \quad \mathcal{O}(N_v^4 N_F) \text{ for } \beta^{-1} \gg \mu - \varepsilon_1$$

- statistical momenta of \hat{H} and \hat{N} for *interacting* system
- similar to response coupled cluster in real time
- excitations equally described by perturbation *and* reference
no leaning tower

summary: resummation

- numerical convolution on $[0, \beta]$ with τ_n grid of size ≈ 12
- numerically difficult but sufficiently accurate: error $< 10^{-5}$
- solves Ansatz of Mandal *et al.* Int. J. Mod. Phys. B **28**,5367 (2003)
- uniform convergence to Almlöf's LT grid as $T \rightarrow 0$:
Chem. Phys. Lett. **176**, 319 (1991). JCP **129**, 044112 (2008).

$$\sum_n w_n e^{-\tau_n \Delta} \approx \frac{1}{\Delta} \quad \text{for occurring excitation energies } \Delta$$

- go to arbitrarily low T !

summary: resummation

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thank you!

other operators

- employ Güttinger (aka. Hellman–Feynman) theorem

$$\left. \frac{d\langle \hat{H}(\lambda \hat{A}) \rangle}{d\lambda} \right|_{\lambda=0} \xrightarrow{\varepsilon \rightarrow 0} \langle \hat{A} \rangle$$

- taking $\langle \hat{H}(\lambda \hat{A}) \rangle = -\partial/\partial\beta \log \mathcal{Z}(\beta, \mu, \lambda \hat{A})$
- include \hat{A} into PT expansion of $\log \mathcal{Z}$ analogously to $T = 0$