Real-Space Stochastic GW Calculations Benchmark on GW100

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Stochastic Implementation of GW Approximation

Within GW approximation,

$$\Sigma\left(\mathbf{r},\mathbf{r}',t\right) = iG(\mathbf{r},\mathbf{r}',t)W(\mathbf{r},\mathbf{r}',t)$$

Approximate Stochastic Resolution of Identity[1] : $I \approx \frac{1}{N_{\bar{\zeta}}}\sum\left|\bar{\zeta}\right\rangle\left\langle\bar{\zeta}\right|$

where $\left|\bar{\zeta}\right\rangle$ is a random orbital which satisfies the condition $\left|\bar{\zeta}(\mathbf{r})\right|^2 = dV$.
Stochastic G:

$$iG(t) = iG(t)I \approx e^{-iH_0 t}[(I-P)\theta(t) - P\theta(-t)]\frac{1}{N_{\bar{\zeta}}}\sum\left|\bar{\zeta}\right\rangle\left\langle\bar{\zeta}\right|$$

$$iG(\mathbf{r},\mathbf{r}',t) \approx \frac{1}{N_{\bar{\zeta}}}\sum\zeta(\mathbf{r},t)\bar{\zeta}(\mathbf{r}')$$

where,

$$\begin{aligned}\zeta(\mathbf{r},t) &= \left\langle\mathbf{r}\middle|e^{-iH_0 t}(I-P)\middle|\bar{\zeta}\right\rangle \qquad t>0\\ &= -\left\langle\mathbf{r}\middle|e^{-iH_0 t}P\middle|\bar{\zeta}\right\rangle \qquad t<0\end{aligned}$$

[1] V Vlček et al., Phys. Rev. B **98**, 075107 (2018)

Decoupling $\mathbf{r}$ and $\mathbf{r}'$ dependence

Diagonal matrix element of self energy for n^{th} DFT orbital ϕ_n,

$$\langle \phi_n | \Sigma(t) | \phi_n \rangle = \int \int \phi_n(\mathbf{r}) i G(\mathbf{r}, \mathbf{r}', t) W(\mathbf{r}, \mathbf{r}', t) \phi_n(\mathbf{r}') d\mathbf{r} d\mathbf{r}'$$

$$\langle \phi_n | \Sigma(t) | \phi_n \rangle \approx \frac{1}{N_{\bar{\zeta}}} \sum_{\bar{\zeta}} \int \phi_n(\mathbf{r}) \zeta(\mathbf{r}, t) u(\mathbf{r}, t) d\mathbf{r}$$

where,

$$u(\mathbf{r}, t) = \int W(\mathbf{r}, \mathbf{r}', t) \bar{\zeta}(\mathbf{r}') \phi_n(\mathbf{r}') d\mathbf{r}'$$

$$u^R(\mathbf{r}, t) = \int d\mathbf{r}' \nu(|\mathbf{r} - \mathbf{r}'|) \bar{\zeta}(\mathbf{r}') \phi_n(\mathbf{r}') \delta(t)$$

$$+ \underbrace{\int d\mathbf{r}'' \nu(|\mathbf{r} - \mathbf{r}''|) \underbrace{\int d\mathbf{r}''' \chi^R(\mathbf{r}'', \mathbf{r}''', t) \underbrace{\int d\mathbf{r}' \nu(|\mathbf{r}''' - \mathbf{r}'|) \bar{\zeta}(\mathbf{r}') \phi_n(\mathbf{r}')}_{\textit{perturbation potential}}}_{\textit{change in density}}}_{\textit{change in Hartree potential}}$$

Procedure of Stochastic GW

- Generate stochastic function $\bar{\zeta}(\mathbf{r})$.
- Perturb all occupied $\phi(\mathbf{r})$ with $v_{pert}(\mathbf{r}) = \int \nu(|\mathbf{r} - \mathbf{r}'|)\bar{\zeta}(\mathbf{r}')\phi_n(\mathbf{r}')d\mathbf{r}'$ and then propagate to calculate response function $u(\mathbf{r}, t)$

$$u^R(\mathbf{r}, t) = \frac{v_H^\lambda(\mathbf{r}, t) - v_H(\mathbf{r})}{\lambda}$$

$$u^R(\mathbf{r}, t) \Rightarrow u(\mathbf{r}, t)$$

- Project and propagate $\bar{\zeta}(\mathbf{r})$ and then calculate, $\int \phi_n(\mathbf{r})\zeta(\mathbf{r}, t)u(\mathbf{r}, t)d\mathbf{r}$.
- Repeat these steps for several $\bar{\zeta}$s and then take the average to get,

$$\langle \phi_n | \Sigma(t) | \phi_n \rangle \approx \frac{1}{N_{\bar{\zeta}}} \sum_{\bar{\zeta}} \int \phi_n(\mathbf{r})\zeta(\mathbf{r}, t)u(\mathbf{r}, t)d\mathbf{r}$$

- Take Fourier transform to get $\Sigma_{nn}(\omega)$.
- $\varepsilon_n^{QP} = \varepsilon_n^{KS} + \left\langle \phi_n \left| \Sigma\left(\omega = \varepsilon^{QP}\right) - v_{\mathrm{xc}} \right| \phi_n \right\rangle$

Decomposition into Stochastic and Embedded Subspace

Decomposing G into embedded and stochastic subspace[2]:

$$G \equiv \tilde{G} + G^{\phi}$$

Embedded supspace:

$$iG^{\phi}\left(r, r', t\right) = \sum_{j} e^{-i\varepsilon_j t}\left[\left(1 - f_j\right)\theta(t) - f_j\theta(-t)\right]\phi_j(r)\phi_j^{*}\left(r'\right)$$

Stochastic subspace:

$$\tilde{G}(\mathbf{r}, \mathbf{r}', t) \approx -\frac{i}{N_{\bar{\zeta}}}\sum \zeta(\mathbf{r}, t)\bar{\zeta}(\mathbf{r}')$$

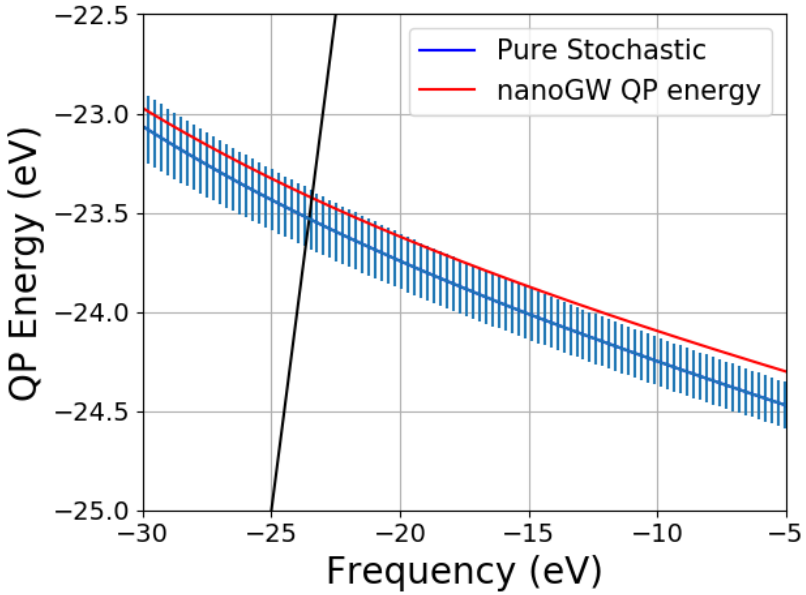
$$\left|\bar{\zeta}\right\rangle = \left(1 - P_{\phi}\right)\left|\bar{\zeta}^{0}\right\rangle$$

where,

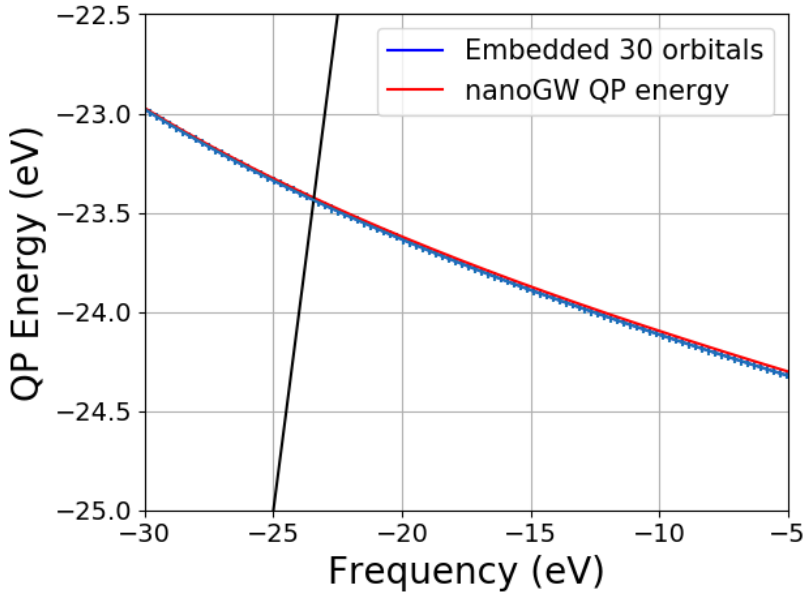
$$P_{\phi} = \sum_{j\in\{\phi\}} \left|\phi_j\right\rangle\left\langle\phi_j\right|$$

[2] M Ramanova and V Vlcěk, J. Chem. Phys. **153**, 134103 (2020)

He atom in a small box : Testing the code



Comparing NanoGW calculations with Stochastic GW without embedding

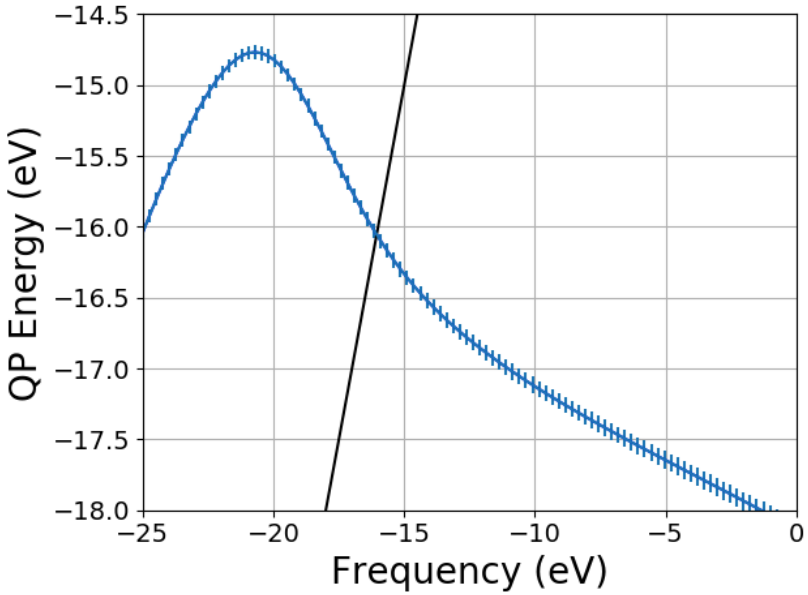


Comparing NanoGW calculations with Stochastic GW with 30 embedded orbitals

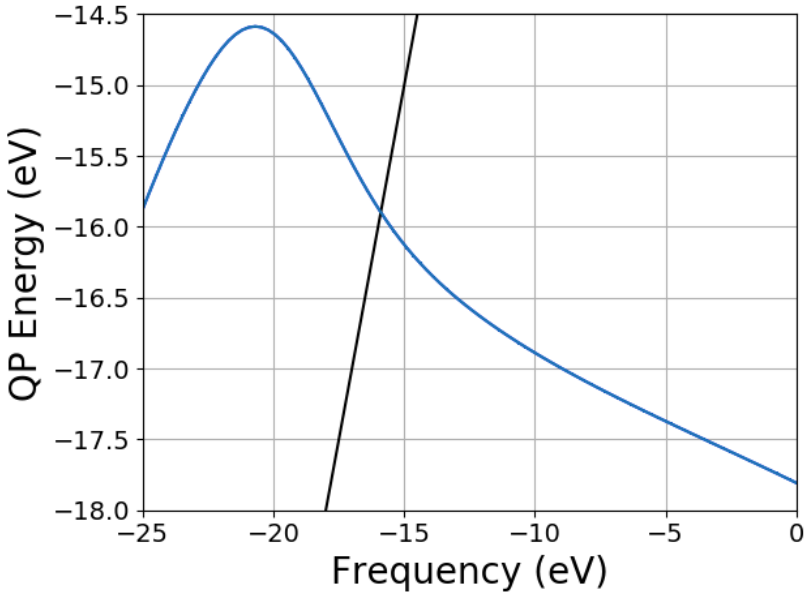
	NanoGW[3]	Stochastic GW	
		Non-embedded	Embedded
Dimension (Bohr)	5	5	5
Grid Spacing (Bohr)	0.3	0.3	0.3
No of Orbitals	2000 (Deterministic)	60000 (Stochastic)	2030 (30 Embedded)
QP Energy (eV)	-23.42	-23.52 (0.15)	-23.44 (0.02)

[3] M. L. Tiago and J. R. Chelikowsky, Phys. Rev. B **73**, 205334 (2006)

Stochastic GW on H_2 molecule



Stochastic GW with 30 embedded orbitals



Stochastic GW with 1000 embedded orbitals

	30 Embedded	1000 Embedded
Dimension (Bohr)	20.4	20.4
Grid Spacing (Bohr)	0.3	0.3
No of Stochastic Orbitals	17600	10400
QP Energy (eV)	**-16.05** (0.05)	**-15.90** (0.01)

NanoGW[4] QP Energy = **-15.75 eV**

[4] W. Gao and J. R. Chelikowsky, J. Chem. Theory Comput. **15**, 5299 (2019)

Stochastic GW on SiH_4 molecule

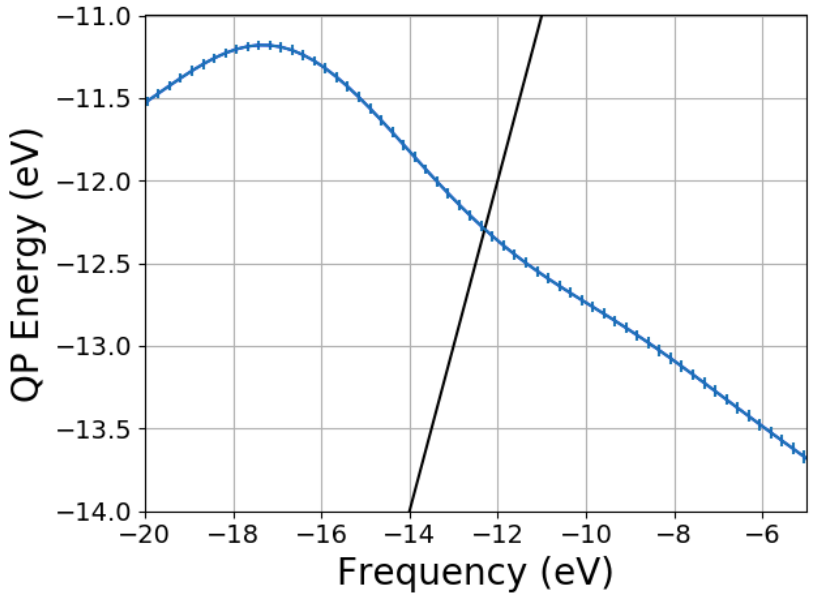


Figure 3: Mean QP Energy computed by Stochastic GW

	Dimension (Bohr)	Grid Spacing (Bohr)	No of Orbitals	QP Energy (eV)
HOMO 1	20.4	0.3	2030	-12.27(0.03)
HOMO 2	20.4	0.3	2030	-12.34(0.04)
HOMO 3	20.4	0.3	2030	-12.27

NanoGW QP Energy = **-12.25 eV** Mean QP Energy = **-12.29(0.03) eV**

Comparing Stochastic, Full Embedded and NanoGW: Phospherene Dimer

P_2:

	Dimension Box/Sphere (Bohr)	Number of Orbitals	QP Energy (eV)
Stochastic	26.4	2000 + 30 embed	-10.54(0.01)
Embedded	26.4	1055 embed	-10.34
NanoGW	25.58	888	-10.32

Comparing Stochastic GW QP energies with NanoGW

Formula	Dimension (Bohr)	No of Orbitals Stoch + Embed	QP Energy (eV)	NanoGW[5] QP Energy (eV)
H_2	20.4	10400 + 1000	-15.90(0.008)	-15.75
He	20.4	10400 + 1000	-23.47(0.03)	-23.20
SiH_4	20.4	2000 + 30	-12.29(0.03)	-12.25
Si_2H_6	20.4	2000 + 30	-10.51(0.03)	-10.32
P_2	26.4	2000 + 30	-10.54(0.01)	-10.32
Na_2	26.4	2000 + 30	-5.31(0.03)	-4.94
Na_4	29.4	2000 + 30	-4.43(0.01)	-4.22
Na_6	29.4	2000 + 30	-4.74(0.02)	-4.35

[5]W. Gao and J. R. Chelikowsky, J. Chem. Theory Comput. **15**, 5299 (2019)

Conclusion and Acknowledgement

- We observe that embedding some DFT eigenstates substantially reduces stochastic error for small molecules.
- We find that using embedded orbitals in the new GW implementation in PARSEC gives quasiparticle eigenvalues in excellent agreement with NanoGW.
- We also observe that stochastic orbitals in *our* implementation seems to systematically underestimate quasiparticle eigenvalues compared to NanoGW.

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