GW Calculations: Total Energies and Input Dependence

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The Green's Function

Causal, One-body, Interacting Green's Function

Defined as:

$$G\left(\mathbf{x}, t, \mathbf{x}', t'\right) = -\mathrm{i}\left\langle \Psi_N^0 \left| \mathcal{T}\left[\hat{\psi}\left(\mathbf{x}, t\right), \hat{\psi}^{\dagger}\left(\mathbf{x}', t'\right)\right] \right| \Psi_N^0 \right\rangle$$

Uses

- Excitation Energies:
  Transform to Lehmann representation
  $G\left(\mathbf{x}, \mathbf{x}', \omega\right)$: poles at addition/removal energies $\Rightarrow$ band structure
- Ground-state Properties:
  Exact expectation value of *any* one-body operator:

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$$-\mathrm{i}\mathrm{Tr}\left[\hat{\mathcal{O}}\hat{G}\left(t, t^+\right)\right] = -\mathrm{i}\sum_{\xi}\int \mathrm{d}\mathbf{r} \lim_{\mathbf{r}\to\mathbf{r}'} \mathcal{O}\left(\mathbf{x}\right) G\left(\mathbf{x}, t, \mathbf{x}', t^+\right)$$

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Galitskii-Migdal Total Energy

- Total energy: a two-body expectation value

$$
\begin{aligned}
E_{\mathrm{GS}} &= -\mathrm{i}\sum_{\xi}\int \lim_{\mathbf{r}'\to\mathbf{r}} \hat{h}_0(\mathbf{x})\, G\left(\mathbf{x}, t, \mathbf{x}', t^{+}\right) \mathrm{d}\mathbf{r} \\
&\quad -\frac{1}{2}\sum_{\xi\xi'}\iint \frac{G\left(\mathbf{x}, t, \mathbf{x}', t, \mathbf{x}, t^{+}, \mathbf{x}', t^{+}\right)}{|\mathbf{r}-\mathbf{r}'|}\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'
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- Transform trace of two-body Green's function:

$$\begin{aligned} &\frac{1}{2}\sum_{\xi\xi'}\iint \frac{1}{|\mathbf{r}-\mathbf{r}'|}\left\langle N\middle|\hat{\psi}^{\dagger}(\mathbf{x},t)\,\hat{\psi}^{\dagger}(\mathbf{x}',t)\,\hat{\psi}(\mathbf{x}',t)\,\hat{\psi}(\mathbf{x},t)\middle|N\right\rangle \mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}' \\ &= \frac{1}{2}\sum_{\xi}\int \mathrm{d}\mathbf{r} \lim_{t'\to t^{+}}\lim_{\mathbf{r}'\to\mathbf{r}}\left[\mathrm{i}\frac{\partial}{\partial t}-\hat{h}_0(\mathbf{x})\right]\left\langle N\middle|\hat{\psi}^{\dagger}(\mathbf{x}',t')\,\hat{\psi}(\mathbf{x},t)\middle|N\right\rangle \end{aligned}$$

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\end{aligned}
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- Exact total energy becomes:

$$
E_{\mathrm{GS}} = -\frac{\mathrm{i}}{2}\sum_{\xi}\int \lim_{\mathbf{r}'\to\mathbf{r}}\lim_{t,t'\to t^{+}}\left[\mathrm{i}\frac{\partial}{\partial t}+\hat{h}_0(\mathbf{x})\right] G\left(\mathbf{x},t,\mathbf{x}',t'\right)\mathrm{d}\mathbf{r}
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- Exact total energy becomes:

$$E_{\mathrm{GS}} = -\frac{\mathrm{i}}{2}\sum_{\xi}\int_{-\infty}^{\mu}\mathrm{d}\omega\int \mathrm{d}\mathbf{r}\lim_{\mathbf{r}'\to\mathbf{r}}\left[\omega+\hat{h}_0(\mathbf{x})\right] G\left(\mathbf{x},\mathbf{x}',\omega\right)$$

Perturbative Approaches: GW Zoo

- Initial State Dependence
  - LDA+G_0W_0 vs. KLI+G_0W_0 **total energies** (Delaney, Rinke, García-González, and Godby)
  - EXX+G_0W_0 **quasiparticle energies** for nitrides (Rinke, Qteish, Neugebauer, Freysoldt, Scheffler)
  - LDA+U+G_0W_0 **quasiparticle energies** for R_2O_3 (Jiang, Gomez-Abal, Rinke, and Scheffler)
- "Beyond" G_0W_0
  - G_0W_0
  - GW (or $scGW$)
  - $G_0W_0\Gamma_0$
  - $GW\Gamma$
- Pseudo-Self-Consistent GW: Iterate a real self energy followed by one-shot G_0W_0
  - Quasiparticle-self-consistent GW (Schilfgaarde + coworkers)
  - Self-consistent COHSEX + GW (Bruneval + Reining group)

Results: Isolated Atoms

Total energies of isolated atoms in Ha/eln:

Atom	HF	LDA	$G_0 W_0$ (LDA)	$G_0 W_0$ (EXX)	"Exact"
He	-1.4304	-1.4171	-1.412	-1.455	-1.452

Correlation energies of isolated atoms in Ha/eln

Atom	HF	LDA	$G_0 W_0$ (LDA)	$G_0 W_0$ (EXX)	"Exact"
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Be	-3.6433	-3.6110	-3.591	-3.678	-3.667

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Be	0.000	0.0323	0.0523	-0.0347	-0.0237

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Ne	-12.855	-12.818	-12.777	-12.843	-12.891

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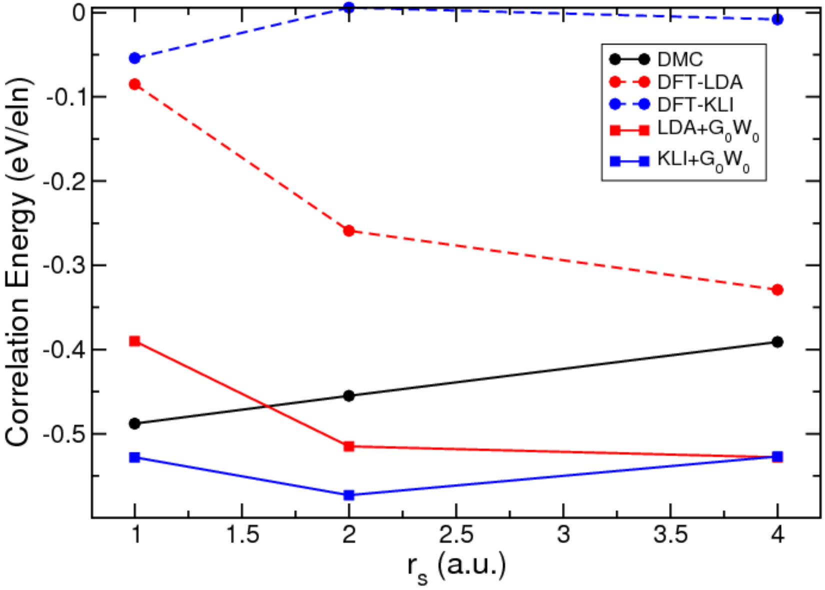
He	0.000	0.0133	0.0184	-0.0246	-0.0216
Be	0.000	0.0323	0.0523	-0.0347	-0.0237
Ne	0.000	0.037	0.078	0.012	-0.036

Results: Jellium Spheres



Results: Jellium Spheres + scGW