Quasiparticle energies for large molecules: a tight-binding based GW approach

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GW2005
Motivation

Goal: fast GW method for molecules

- Separate N,N± DFT calculations necessary for reasonable IP, EA values
- QP energies as input for transport calculations in molecular devices
- GW+BS where TDDFT fails (CT transitions)

⇒ atomic orbital basis + integral approx.
\[ \epsilon_{i}^{QP} = \epsilon_{i}^{DFT} + Z_{i} \langle \psi_{i}^{DFT} | \Sigma(\epsilon_{i}^{DFT}) - \nu_{xc} | \psi_{i}^{DFT} \rangle \]
DFT wave function and energies: $\epsilon^\text{DFT}_i, \psi^\text{DFT}_i$

From DFTB (Density-functional-theory based Tight-Binding) method

- **Minimal AO basis:** $\psi_i(r) = \sum_\mu c_{\mu i} \varphi_\mu(r - R_A)$
- **Density divided into reference density ($\rho_0$) and fluctuation:**
  $\rho = \rho_0 + \delta \rho$
- **Total energy:**

\[
E_{\text{tot}} = \sum_i \sum_{\mu \nu} c_{\mu i} H^0_{\mu \nu}[\rho_0] c_{\nu i} + \sum_{AB} \gamma_{AB} \Delta q_A \Delta q_B + U_{\text{rep}}
\]

- **Two-center approximation**, matrix elements calculated not fitted
- $\gamma_{AB}$ represents e-e interaction (including xc)
Exchange part of self energy: $\Sigma_x$

Basis for two-point functions $F_{\mu}(r)$ is chosen different from basis to construct DFT orbitals

$$F_{Al}(r) = \frac{1}{2l+1} \sum_{m=-l}^{m=l} |\phi_{Alm}(r)|^2, \quad \phi_\mu(r)\phi_\nu(r) \approx \frac{1}{2} S_{\mu\nu} [F_{\mu}(r) + F_{\nu}(r)]$$

Mulliken approximation used to transform 4-center into 2-center integral

$$\langle \psi_i | \Sigma_x | \psi_i \rangle = - \sum_j \sum_{i}^{occ} c_{\mu i} c_{v j} c_{a i} c_{\beta j} \int \int \frac{\phi_\mu(r)\phi_\nu(r)\phi_{\alpha}(r')\phi_{\beta}(r')}{|r - r'|} dr dr' \approx - \sum_{j\alpha\beta} q_{ij}^{\alpha\beta} [v]_{\alpha\beta} q_{ij}^{\alpha\beta},$$

$$q_{ij}^{\alpha\beta} = \frac{1}{2} \sum_{m=-l}^{m=l} \sum_{\nu} \left( c_{\mu i} c_{v j} S_{\mu\nu} + c_{v i} c_{\mu j} S_{\nu\mu} \right) \quad [v]_{\alpha\beta} = \int \int \frac{F_{\alpha}(r)F_{\beta}(r')}{|r - r'|} dr dr'$$
Exchange part of self energy: $\Sigma_x$

\[
[v]_{\alpha\beta} = \int \int \frac{F_{\alpha}(r)F_{\beta}(r')}{|r - r'|} dr dr' \approx \gamma_{\alpha\beta}(|R_A - R_B|, U_{\alpha}^{ee}, U_{\beta}^{ee})
\]

Interpolation between atomic integral $U_{ee}$ and $1/R$ for large distances

All onsite exchange-integrals numerically evaluated
Correlation part of self energy: $\Sigma_c$

Polarization simplified by Mulliken approximation, overlap $\tilde{S}_{\mu\bar{a}}$ actually never needed

$$[P(\omega)]_{\mu\bar{\nu}} = \sum_{kl} \left( \sum_{\bar{a}} \tilde{S}_{\mu\bar{a}} q_{\bar{a}l}^{kl} \right) \left( \sum_{\bar{\beta}} q_{\bar{\beta}l}^{kl} \tilde{S}_{\bar{\beta}\bar{\nu}} \right) \left[ \frac{f_k - f_l}{\epsilon_k^{\text{DFTB}} - \epsilon_l^{\text{DFTB}} + \omega + i0^+} \right]$$

Microscopic dielectric function and screened Coulomb interaction

$$[\epsilon(\omega)] = \tilde{S} - [\nu] \tilde{S}^{-1} [P(\omega)] \quad \Rightarrow \quad [W(\omega)] = \tilde{S} [\epsilon(\omega)]^{-1} [\nu]$$

Simple plasmon pole model for $W$
Contribution due to $v_{xc}$

Expansion around reference density, zeroth order can be tabulated

$$\langle \psi_i | v_{xc}(\rho) | \psi_j \rangle = \sum_{\mu \nu} c_{\mu i} c_{\nu j} \langle \varphi_\mu | v_{xc}(\rho_0) | \varphi_\nu \rangle + \int \int d^3r d^3r' \psi_i(r) \frac{\partial v_{xc}(r)}{\partial \rho(r')} \Delta \rho(r') \psi_j(r)$$

$$\simeq \sum_{\mu \nu} c_{\mu i} c_{\nu j} \langle \varphi_\mu | v_{xc}(\rho_0) | \varphi_\nu \rangle + \sum_{\bar{a} \bar{b}} q_{\bar{a}}^{ij} [\partial v_{xc}/\partial \rho]_{\bar{a} \bar{b}} \Delta q_{\bar{b}}$$

Matrix elements of $\partial v_{xc}/\partial \rho$ from interpolation function
### Final results: benzene

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The polyacene series: QP versus DFT gap
**Sodium cluster**

First-principles calc.:

Summary

- Parameter free GW method for large molecules (extension to other elements easy)
- Good agreement with first principles for frontier orbitals
- \( \sigma \)-orbitals not convincing
- First principles calc. anthracene: 10200 s, GW-DFTB: < 1 s, also scaling < \( N^4 \)
- Implementation valid for periodic systems but not optimal (k-point sampling)
- Implementation of Bethe-Salpeter equation under way
Thanks

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