

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

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*GW*2005

Motivation

Goal: **fast** GW method for **molecules**

- Seperate $N, N\pm$ 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)

$\Rightarrow$ atomic orbital basis + integral approx.

$$\epsilon_i^{\text{QP}} = \epsilon_i^{\text{DFT}} + Z_i \langle \psi_i^{\text{DFT}} | \sum (\epsilon_i^{\text{DFT}}) - v_{\text{xc}} | \psi_i^{\text{DFT}} \rangle$$

DFT wave function and energies: $\epsilon_i^{\text{DFT}}, \psi_i^{\text{DFT}}$

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

- Minimal AO basis: $\psi_i(\mathbf{r}) = \sum_{\mu} c_{\mu i} \phi_{\mu}(\mathbf{r} - \mathbf{R}_A)$
- Density divided into reference density (ρ_0) and fluctuation:
 $\rho = \rho_0 + \delta\rho$
- Total energy:

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

- Two-center approximation, matrix elements calculated not fitted
- V_{AB} represents e-e interaction (including xc)

Exchange part of self energy: Σ_x

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

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

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

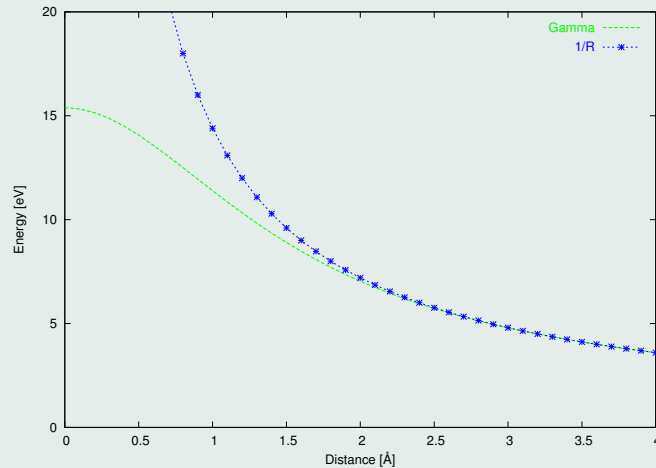
$$\langle \psi_i | \Sigma_x | \psi_i \rangle = - \sum_j^{\text{occ}} c_{\mu i} c_{\nu j} c_{\alpha i} c_{\beta j} \iint \frac{\varphi_{\mu}(r) \varphi_{\nu}(r) \varphi_{\alpha}(r') \varphi_{\beta}(r')}{|r - r'|} dr dr' \approx - \sum_{j \bar{\alpha} \bar{\beta}} q_{\bar{\alpha}}^{ij} [v]_{\bar{\alpha}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

$$q_{\bar{\mu}}^{ij} = \frac{1}{2} \sum_{m=-l}^l \sum_{\nu} \left(c_{\mu i} c_{\nu j} S_{\mu\nu} + c_{\nu i} c_{\mu j} S_{\nu\mu} \right) \quad [v]_{\bar{\alpha} \bar{\beta}} = \iint \frac{F_{\bar{\alpha}}(r) F_{\bar{\beta}}(r')}{|r - r'|} dr dr'$$

Exchange part of self energy: Σ_x

$$[v]_{\bar{\alpha}\bar{\beta}} = \iint \frac{F_{\bar{\alpha}}(\mathbf{r})F_{\bar{\beta}}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \approx \gamma_{\bar{\alpha}\bar{\beta}}(|\mathbf{R}_A - \mathbf{R}_B|, U_{\bar{\alpha}}^{ee}, U_{\bar{\beta}}^{ee})$$

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



All onsite exchange-integrals numerically evaluated

Correlation part of self energy: Σ_c

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

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

Microscopic dielectric function and screened Coulomb
interaction

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

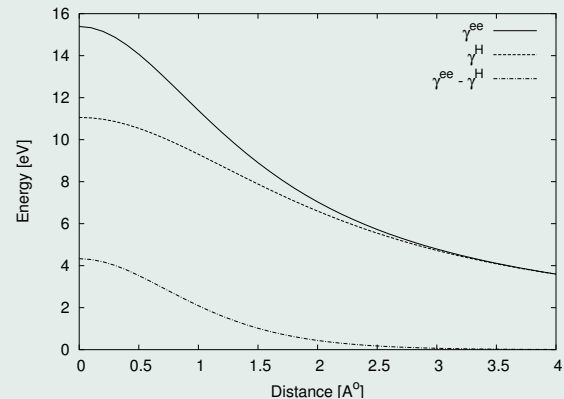
Simple plasmon pole model for W

Contribution due to v_{xc}

Expansion around reference density, zeroth order can be tabulated

$$\begin{aligned} \langle \psi_i | v_{xc}(\rho) | \psi_j \rangle &= \sum_{\mu\nu} c_{\mu i} c_{\nu j} \langle \phi_\mu | v_{xc}(\rho_0) | \phi_\nu \rangle + \iint d^3r d^3r' \psi_i(r) \frac{\partial v_{xc}(r)}{\partial \rho(r')} \Delta \rho(r') \psi_j(r) \\ &\approx \sum_{\mu\nu} c_{\mu i} c_{\nu j} \langle \phi_\mu | v_{xc}(\rho_0) | \phi_\nu \rangle + \sum_{\bar{a}\bar{b}} q_{\bar{a}}^{ij} [\partial v_{xc} / \partial \rho]_{\bar{a}\bar{b}} \Delta q_{\bar{b}} \end{aligned}$$

Matrix elements of $\partial v_{xc} / \partial \rho$
from interpolation function

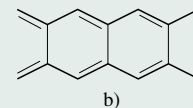
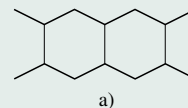
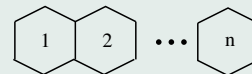
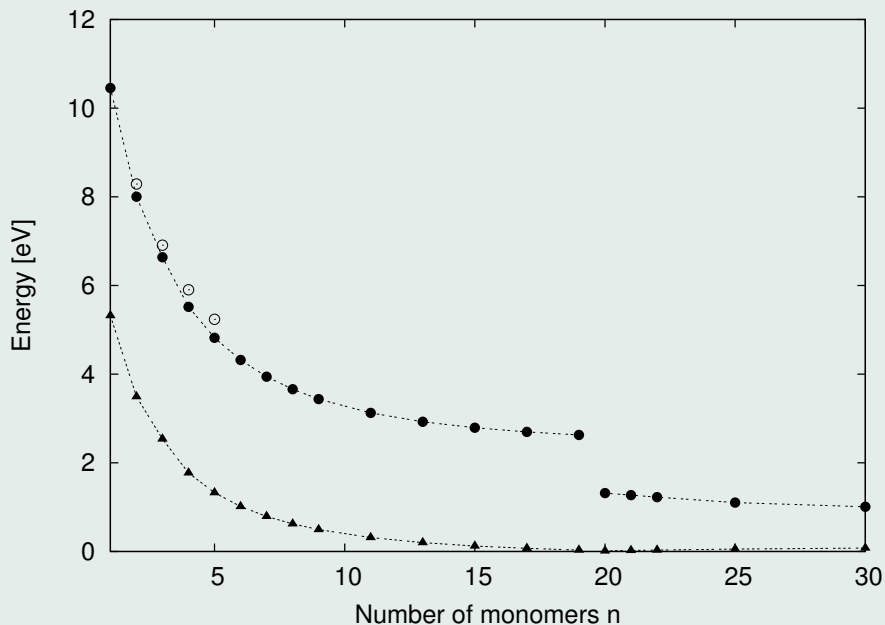


Final results: benzene

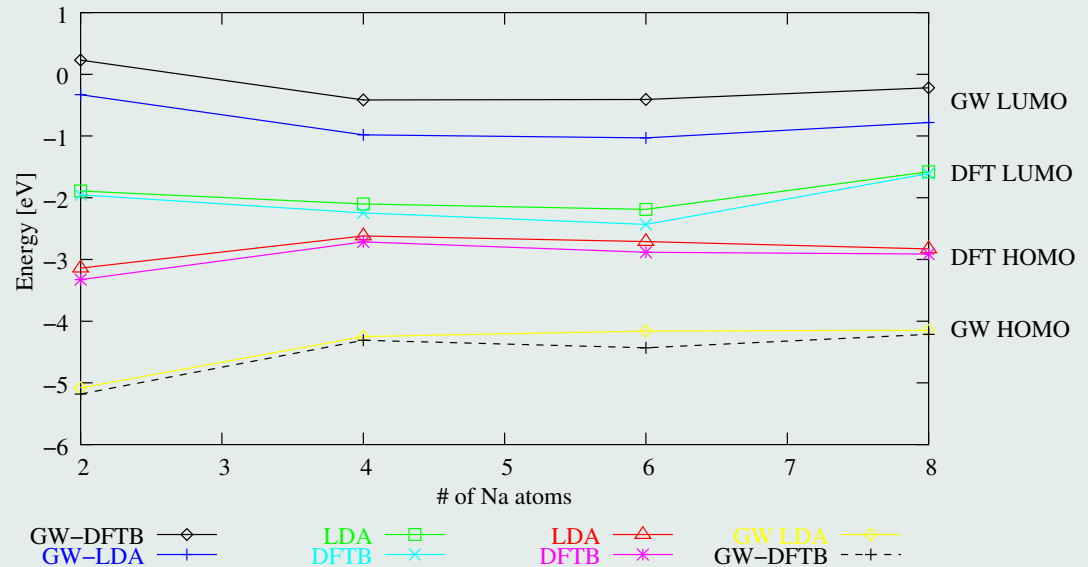
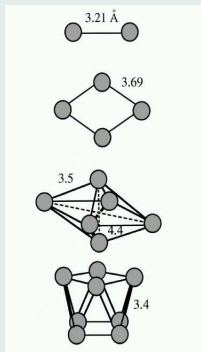
State	Sym.	ϵ^i		v_{xc}^i		Σ_x^i	
		GTO	DFTB	GTO	DFTB	GTO	DFTB
A_{2u}	π	-9.37	-8.95	-12.82	-12.39	-17.15	-16.35
E_{2g}	σ	-8.34	-7.71	-15.05	-12.25	-19.49	-15.62
E_{1g}	π	-6.59	-6.64	-13.03	-12.30	-15.61	-14.98
E_{2u}	π^*	-1.30	-1.32	-12.64	-11.72	-7.58	-7.41
B_{2g}	π^*	0.92	2.29	-6.96	-11.19	-2.89	-6.33

State	Sym.	Σ_c^i		ϵ_{QP}^i	
		GTO	DFTB	GTO	DFTB
A_{2u}	π	2.03	2.47	-11.67	-10.45
E_{2g}	σ	1.86	1.41	-10.92	-9.67
E_{1g}	π	0.59	0.87	-8.58	-8.46
E_{2u}	π^*	-1.74	-0.99	2.01	2.00
B_{2g}	π^*	-2.31	-2.84	2.67	4.31

The polyacene series: QP versus DFT gap



Sodium cluster



First-principles calc.:

S. Ishii, K. Ohno, Y. Kawazoe, and S.G. Louie, Phys. Rev. B **63**, 155104, (2001).

Summary

- Parameter free *GW* method for large molecules (extension to other elements easy)
- Good agreement with first principles for frontier orbitals
- σ -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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