Many-body dispersion interactions between semiconducting wires

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Hückel chains

Interactions between two parallel infinite wires.

Two-band Hamiltonian:

\[ H = \sum_{i}^{n} (\beta a_{2i}^{\dagger} a_{2i-1} + \beta' a_{2i+1}^{\dagger} a_{2i} + h.c.) \]  

Models interactions between \((H_2)_n\) chains or \(\pi\)-conjugated polyenes.

Band-gap is given by

\[ \Delta E_g = 2(\beta - \beta') \]
Dispersion energy:

\[
E^{(2)}_{\text{disp}} = \sum_{i \in A, j \in B} \sum_{a \in A, b \in B} \frac{\left| \langle ij | r_{12}^{-1} | ab \rangle \right|^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}.
\]  

Large finite-size effects: \( k \)-point sampling equivalent to a crystal cell with 16802 sites.
Infinite, parallel chains with gap: $\Delta E_g = 2\beta$

\[ E_{\text{disp}}^{(2)} / |\beta| \propto z^{-5.00} \]
Infinite, parallel chains with gap: $\Delta E_g = 0$

<table>
<thead>
<tr>
<th>System</th>
<th>Metals</th>
<th>Insulators</th>
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<td>1-D</td>
<td>$-R^{-2} \ln(KR)^{-3/2}$</td>
<td>$-R^{-5}$</td>
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<tr>
<td>2-D</td>
<td>$-R^{-5/2}$</td>
<td>$-R^{-4}$</td>
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- Verified using DMC calculations on the 1-D and 2-D HEG by Drummond & Needs (PRL 99, (2007)).
Infinite, parallel chains with gap: $\Delta E_g = 2(\beta - \beta')$
SAPT(DFT) Interaction of \((\text{H}_2)_n\) chains using SAPT(DFT) (symmetry-adapted perturbation theory based on DFT).

Finite chains: \(n = 2, 4, 8, 16, 32\)
- Control HOMO–LUMO gap using bond alternation. \(\eta = y/x\).
- Gap goes from 10 eV (smallest chain) to 1 eV.
SAPT(DFT) dispersion is calculated using the generalized Casimir-Polder expression (Longuet-Higgins (1965)):

\[
E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \int_{0}^{\infty} dw \int \frac{\alpha_A(r_1, r'_1; i\omega)\alpha_B(r_2, r'_2; i\omega)}{|r_1 - r_2||r'_1 - r'_2|} dr_1 dr'_1 dr_2 dr'_2
\]

Where \(\alpha(r, r'; \omega)\) is the frequency-dependent density susceptibility function (FDDS).

Advantages of perturbation theory: separate out the dispersion from the long-range electrostatics.
Bond alternation: $\eta = y/x = 2$, $E_g = 0.366$ a.u.
Bond alternation: $\eta = y/x = 1$, $E_g = 0.057$ a.u.
Bond alternation: $\eta = y/x$
No single power law.

Two regions (distances in a.u.):

\[ z^{-6} : \text{for } z \gg L \]

\[ z^{-x} : x < 5 \text{ for } 6 < z < 20. \]

The anomalous power law occurs at physically important separations.

Enhanced dispersion: At \( z = 40 \) a.u. (roughly half chain length), two orders of magnitude between chains with \( \eta = 1 \) and \( \eta = 2 \).

Enhancement orders of magnitude less than for the Hückel chains: importance of screening.
Non-additivity of total polarizabilities can explain three order of magnitude enhancement at very long range. Longitudinal static polarizabilities for \((H_2)_32\) chains:

\[
\frac{\alpha(\eta = 1.0)}{\alpha(\eta = 2.0)} = \frac{11589}{415} = 28
\]  \hspace{1cm} (4)

Dispersion energy depends quadratically on the polarizability.

- But extrapolation to intermediate distances overestimates dispersion by orders of magnitude.
- Failure of additivity.
- Not damping or retardation.
- Severe finite-size effects…
At the time, I had been working on very accurate multipole expansions for the dispersion energy using WSM method (available in the CAMCASP program):

\[
E_{\text{disp}}^{(2)} = - \sum_{a,b} \left( \frac{C_{6}^{ab}}{R_{ab}^{6}} + \frac{C_{7}^{ab}}{R_{ab}^{7}} + \frac{C_{8}^{ab}}{R_{ab}^{8}} + \cdots \right)
\]  

Based on density-response functions calculated using linear-response TD-DFT.

Consistent with SAPT(DFT) dispersion energies.

Very accurate models. R.m.s. errors of 0.5 kJ mol\(^{-1}\) across large energy ranges (-40 to 0 kJ mol\(^{-1}\)).
Pyridine dimer: WSM dispersion models (damped).
Multipole Expansion

- For $z > 6$ a.u.: Density overlap is negligible. So multipole expansion should be valid.

- Usually we take this to mean that

$$E_{\text{disp}}^{(2)} = -\sum_{a,b} \frac{C_{6}^{ab}}{R_{ab}^{6}}.$$  

- But this cannot yield an effective power law with exponent less than 5.

- Nor can the more general expression:

$$E_{\text{disp}}^{(2)} = -\sum_{a,b} \left( \frac{C_{6}^{ab}}{R_{ab}^{6}} + \frac{C_{7}^{ab}}{R_{ab}^{7}} + \frac{C_{8}^{ab}}{R_{ab}^{8}} + \cdots \right)$$

where each coefficient is angular dependent.
Longuet-Higgins (1965) expression for the dispersion energy:

\[
E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \int_0^\infty dw \int \frac{\alpha_A(r_1, r_1'; iw)\alpha_B(r_2, r_2'; iw)}{|r_1 - r_2||r_1' - r_2'|} dr_1 dr_1' dr_2 dr_2'
\]

Taylor expansion (systems separated by \( R \)): Leading order term is usually written as the dipole-dipole interaction:

\[
\frac{1}{|r - r'|} = -\hat{\mu}_\alpha \frac{3R_\alpha R_\beta - R^2 \delta_{\alpha\beta}}{R^5} \hat{\mu}_\beta
\]  

But this is insufficient. It leads to the usual \(-C_6 R^{-6}\) form.

Generalize:

\[
\frac{1}{|r - r'|} = \hat{Q}_t^A T_{tu}^{AB} \hat{Q}_u^B
\]  

where \( t = 00, 10, 11c, 11s, \ldots \) label the rank of the multipole moment operators.
A T-function of ranks $l$ and $l'$ behaves like $R^{-l-l'-1}$.

Distribute: For extended systems use multiple centres:

$$\frac{1}{|r - r'|} = \sum_a \sum_b \hat{Q}^a_t T^{ab}_{tu} \hat{Q}^b_u. \quad (10)$$

Inserting this in the Longuet-Higgins expression gives:

$$E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \sum_{a,a'} \sum_{b,b'} T^{ab}_{tu} T^{a'b'}_{t'u'} \int_0^\infty \alpha^{aa'}_{tt'}(iw) \alpha^{bb'}_{uu'}(iw) dw \quad (11)$$

where the non-local polarizabilities are defined as

$$\alpha^{aa'}_{tt'}(\omega) = \iint \hat{Q}^a_t(r) \alpha(r, r'; \omega) \hat{Q}^{a'}_{t'}(r') dr dr' \quad (12)$$

This is the correct multipole expansion for the dispersion. For details see Stone `The Theory of Intermolecular Forces’ (1996).
To obtain the usual expansion we must *localize* the non-local polarizabilities. This is usually done by another multipole expansion, but there are other methods.

The result is that only terms involving the same site remain.

This is an approximation that assumes that

\[ \alpha^{aa'} \sim e^{-\gamma|R_{aa'}|}, \]  

(13)

where \( \gamma \sim 1 \).

When this is true, the localization is valid and we get

\[
E_{\text{disp}}^{(2)} = -\frac{1}{2\pi} \sum_a \sum_b T_{tu}^{ab} T_{t'u'}^{ab} \int_0^\infty \alpha_{tt'}^{a}(iw)\alpha_{uu'}^{b}(iw) dw \\
= - \sum_a \sum_b \left( \frac{C_6^{ab}}{R_6^{ab}} + \frac{C_7^{ab}}{R_7^{ab}} + \frac{C_8^{ab}}{R_8^{ab}} + \cdots \right)
\]
Pyridine dimer: WSM dispersion models (damped).
What are the non-local polarizabilities?

- The lowest rank polarizability is $\alpha_{00,00}^{aa'}$.

- If $V^a$ is the potential at site $a$, the change in charge at site $a$ is given by

$$\Delta \hat{Q}_a^a = - \sum_{a'} \alpha_{00,00}^{aa'} (V^{a'} - V^a).$$  \hspace{1cm} (14)

- So such terms describe the flow of charge in response to a potential. They are therefore termed charge-flow polarizabilities.

- These are the analogue of the low (zero) frequency plasmon modes.

- They contribute $R^{-2}$ terms to the dispersion energy.
Sum rule: Charge conservation requires that

\[ \int \alpha(r, r' \omega) dr' = 0, \]  \hspace{1cm} (15)

and this results in the charge-flow sum rule

\[ \sum_{a'} \alpha_{t,00}^{aa'} = 0. \]  \hspace{1cm} (16)
Charge-flow contribution to the dispersion energy:

\[ E^{(2)}_{\text{disp}}(00,00) = -\frac{1}{2\pi} \sum_{aa',bb'} \int_0^\infty \frac{\alpha_{00,00}^{aa'}(iw)\alpha_{00,00}^{bb'}(iw)}{R_{ab}R_{a'b'}} dw \]

(17)

- \( z \leq L_c \): Large \( R^{-2} \) contribution.
- \( L_c \ll z < L \): Charge-fluctuations small compared to \( R_{ab} \) and only \( R_{a'b'} \) close to \( R_{ab} \) contribute...(see fig)...

\[ \text{Graphite} \]

3-body
\[ L_c \ll z < L: \]

\[
E_{\text{disp}}^{(2)}(00,00) = -\frac{1}{2\pi} \sum_{aa',bb'} \frac{1}{R_{ab} R_{a'b'}} \int_0^\infty \alpha_{00,00}^{aa'}(iw) \alpha_{00,00}^{bb'}(iw) dw
\]

\[
\approx -\frac{1}{2\pi} \sum_{ab} \frac{1}{R_{ab} R_{ab}}
\int_0^\infty \left( \sum_{a'} \alpha_{00,00}^{aa'}(iw) \right) \left( \sum_{b'} \alpha_{00,00}^{bb'}(iw) \right) dw
\]

\[
= 0 \quad (18)
\]

But higher-order terms are non-zero.
\[ L \ll z: \text{ In this limit both } R_{ab} \text{ and } R_{a'b'} \text{ can be expanded in a multipole expansion about } \mathcal{R} = (0, 0, z): \]

\[ R^{-1}_{ab} = \left| \mathcal{R} - (r_a - r_b) \right|^{-1} = \left| \mathcal{R} - r_{ab} \right|^{-1} \approx z^{-1} - \frac{1}{2} r_{ab}^2 z^{-3} \]

\[ \text{Use sum-rule.} \]

\[ E^{(2)}_{\text{disp}}(00, 00) \approx -\frac{1}{2\pi} \frac{1}{4z^6} \sum_{aa'} \sum_{bb'} r_{ab}^2 r_{a'b'}^2 \]

\[ \times \int_0^\infty \alpha_{00,00}^{aa'}(i\omega)\alpha_{00,00}^{bb'}(i\omega) d\omega \]

\[ \equiv -\frac{C_6(00, 00)}{z^6}. \quad (19) \]

How do the charge-flow terms behave for the chains?
Charge-flow polarizability matrix: (H2)32 : 2Re

\[
\text{ln|Abs(\alpha_{(0,0)})|} \quad [\text{a.u.}]
\]
Charge-flow polarizability matrix: (H2)32 : 1.5Re
Charge-flow polarizability matrix: $\langle H_2 \rangle_{32} : 1.25 \text{Re}$
Charge-flow polarizability matrix: (H2)32 : 1Re
Hückel chains

SAPT(DFT)

Physical Picture

Polarizabilities

Summary

Graphite

3-body

η = 1.0

η = 2.0

 Charge-flow only

Up to dipole-dipole

SAPT(DFT)
Angyan (2007,2009) has shown that the charge-flow polarizabilities are related to the the XC-hole by relating the density autocorrelation function

\[ S(r, r') = \rho(r)\delta(r - rp) + \rho(r) h_{xc}(r, r') \]  \hspace{1cm} (20)

to the FDDS using the Unsold approximation:

\[ \alpha(r, r'; 0) = \frac{\pi}{\hbar \omega} S(r, r'). \]  \hspace{1cm} (21)

Therefore,

\[ \alpha_{00,00}^{aa'} = \int_{\Omega_a} \int_{\Omega_{a'}} \alpha(r, r'; 0) dr dr' \]

\[ = \frac{\pi}{\hbar \omega} \left( N_a \delta_{aa'} + \int_{\Omega_a} \rho(r) \int_{\Omega_{a'}} h_{xc}(r, r') dr dr' \right) \]
Analysis

- Failure of additivity (and the pair-wise $-C_6/R^6$ model) as the gap decreases and system length increases.
- Require explicit non-local terms. This non-locality is contained in the full density response function $\alpha(r, r'; \omega)$.
- The non-local charge-flow terms do two things: (1) change the power-law for the interaction, and (2) enhance the dispersion interaction.
- Is this really important? What about carbon systems...?
- What about 2-D systems like graphene?
PAHs: SAPT(DFT) Pair Potential

\[ U_{ab} = G \exp \left[ -\alpha_{ab} \left( R_{ab} - \rho_{ab}(\Omega_{ab}) \right) \right] - f_6(R_{ab}) \frac{C_{6,iso}}{R_{ab}^6} + E_{elst}(\text{model}) \]

- Benzene dimer interaction energies (500 geometries).
- Larger PAH dimers: naphthalene, anthracene, pyrene.
- Validated on coronene dimers (not included in the fit).
Graphene & graphite Estimate of *additive* exfoliation energy of graphite by extrapolation:

\[
\frac{E_{\text{bind}}(m)}{m} = \frac{am}{b + m}
\]  

(22)
Introduction
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3-body

- experiment
- theory

- Girifalco
  - Lattice summation

- Girifalco
  - wetting of graphite

- conversion error

- DiVincenzo
- DFT+Thomas Fermi

- Zacharia polyanaromatics

- Ortmann
- GGA+semiemp. vdW

- Spanu - DMC

- Gould -- LDA/GGA + semiemp. corr.
- Hasegawa -- DFT + semiemp. corr.
- Donchev -- QMPFF
- Ziambaras -- general DFT-vdW

- Zhechkov
- DFTP+a posteriori vdW

- PAH clusters

- Schabel
- DFT-LDA

- Telling
- DFT-LDA

- Benedikt
- collapse of CNT

- Rydberg
- layered DFT-vdW

- Charlier
- DFT-LDA


- $E_{\text{ex}}$ (meV/atom)
3-body dispersion For 3 atoms: Axilrod–Teller–Muto:

\[ E_{\text{disp}}^{(2)}(3 - \text{body}) = C_9 \frac{1 + 3 \cos \hat{A} \cos \hat{B} \cos \hat{C}}{R_{AB}^3 R_{AC}^3 R_{BC}^3} \sim \frac{C_9}{R^9} \] (23)
Generalization for non-local, anisotropic, polarizabilities based on expression given by Strogryn (1971):

\[
E_{\text{disp}}^{\text{asymp}}[3] = \frac{\hbar}{\pi} \int_0^\infty \alpha_{\alpha\beta}(i\omega)\alpha_{\gamma\delta}(i\omega)\alpha_{\epsilon\phi}(i\omega) d\omega T_{\gamma\beta} T_{\epsilon\delta} T_{\alpha\phi}
\]

(24)
Infinite, parallel chains with finite gap

Length scale: $R$

$R$

$R$
Infinite, parallel chains with finite gap

Length scale: \( R \)

Select section of order \( R \).
Infinite, parallel chains with finite gap

Interaction of blue atom with others is:

\[
\frac{C_9}{R^9} \times (R \times R)
\]

(25)
Infinite, parallel chains with finite gap

But there are order $R$ blue atoms, so interaction between the bits in the box is:

$$\frac{C_9}{R^9} \times (R \times R) \times R$$  \hspace{1cm} (26)
Infinite, parallel chains with finite gap

And interaction per unit length is:

\[
\frac{C_9}{R^9} \times (R \times R) \times \frac{R}{R} = \frac{C_9}{R^7}
\]  

(27)
$E^{(2)}_{\text{disp}}(3\text{-body}) / n$ / a.u.

$\eta = 2.0$

$\eta = 1.0$

$z = 4.48$

$z = 6.80$

$z = 8.98$

$z = 8.93$
A. J. Misquitta, J. Spencer, A. J. Stone and A. Alavi

All calculations were performed with the CamCASP suite of programs. Download: http://www-stone.ch.cam.ac.uk/programs.html.

