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Groundstate dispersion interaction between π-conjugated polymers

William Barford[a] and Xibai Xu[b]
Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom

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The line-dipole approximation is used to investigate the scaling of the groundstate dispersion interaction, E_W, between parallel conjugated polymers of length L and transverse separation D. Both a second-order perturbation theory calculation using the Mott-Wannier exciton model of excited states and a semiclassical analysis of distributed dipoles indicate that at $L \sim D$ there is a crossover from the point-dipole approximation result of $E_W \sim L^2/D^6$ for $L \ll D$ to the thermodynamically expected result of $E_W \sim L/D^5$ for $L \gg D$. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2822127]

I. INTRODUCTION

The dispersion (or London) interaction[1] between a pair of closed shell molecules separated by a distance D is

$$E_W = -\frac{3}{2(4\pi\epsilon_0)^2}\left(\frac{I_A I_B}{I_A + I_B}\right)\frac{\alpha_A \alpha_B}{D^6}, \tag{1}$$

where α_X is the polarizability and I_X is the ionization energy of molecule X. Since the Kuhn oscillator sum rule implies that the polarizability scales as N, where N is the number of electrons in the molecule, the London result therefore predicts that the interaction energy scales as N^2. In the asymptotic limit of the molecular size much larger than the molecular separation this result is evidently unphysical, as it implies that matter can be spontaneously created. Asymptotically the interaction energy should scale as N. The origin of this incorrect asymptotic prediction arises from the application of the point-dipole approximation to the interaction between a pair of molecules. Evidently, for molecules whose physical size exceeds the separation between them this approximation is invalid. This observation is particularly pertinent to π-conjugated chromophores and polymers, where the conjugation length is typically much larger than the separation of nearest neighbor molecules.

Besides these physical reasons for expecting a crossover in the behavior of E_W as a function of separation, there are also mathematical reasons for expecting such a crossover arising from the expression for E_W derived from perturbation theory. As described in the next section, according to second-order perturbation theory the expression for E_W involves the intermolecular exciton transfer integral. As was shown numerically in Refs. 2–5 and analytically in Ref. 6, the exciton transfer integral scales as L for $L \ll D$ and as $L^{-\nu}$ for $L \gg D$ (with $\nu=1$ in the plane-wave approximation),[6] where L is the polymer length. Mathematically, therefore, it is also reasonable to expect that there will be a crossover in the scaling behavior of E_W at $L \sim D$.

The groundstate dispersion interaction between large *saturated* molecules can be calculated assuming *pairwise additive* London interactions. In this case, as shown by Salem in 1962,[7]

$$E_W \sim -\frac{L}{D^5}\left(3\tan^{-1}(L/D) + \frac{L/D}{1+(L/D)^2}\right), \tag{2}$$

satisfying the physical constraints discussed above.

A noninteracting description of π-electrons in *unsaturated* π-conjugated systems was adopted by Coulson and Davies,[8] and Haugh and Hirschfelder[9] to predict the groundstate dispersion interactions, while Sternlicht[10] adopted a Luttinger liquid approach to describe the dispersion interactions between metallic systems of interacting electrons.

In this paper we calculate the dispersion interaction between semiconducting π-conjugated polymers using the line-dipole approximation,[6,11,12] which assumes (as can be rigorously justified for polymer separations much larger than the monomer size) that the polymeric transition dipole moment is distributed as a coherent sum of dipoles over the entire chain. In the next section we develop a second-order perturbation theory based on the Mott-Wannier exciton model of conjugated polymers. In the following section we confirm these predictions via a semiclassical calculation that does not assume pairwise additive interactions. As expected, in both cases we show that for $L \ll D$, $E_W \sim L^2/D^6$, while for $L \gg D$, $E_W \sim L/D^5$.

II. PERTURBATION THEORY CALCULATION OF THE GROUNDSTATE INTERACTION

We consider an idealized "polyacetylene" geometry of two parallel conjugated polymers labeled 1 and 2 of length L and separated by a transverse distance D, as illustrated in Fig. 1. The groundstate is denoted by $|A\rangle$. In the absence of intermolecular interactions $|A\rangle$ is the product state,

$$|A\rangle = |\mathrm{GS}\rangle_1 |\mathrm{GS}\rangle_2, \tag{3}$$

where $|\mathrm{GS}\rangle_m$ represents the groundstate of polymer m.

To second order in perturbation theory the change in the groundstate energy arising from the intermolecular Coulomb interactions is

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[a] Electronic mail: william.barford@chem.ox.ac.uk.
[b] Electronic mail: xibai.xu@stx.oxon.org.

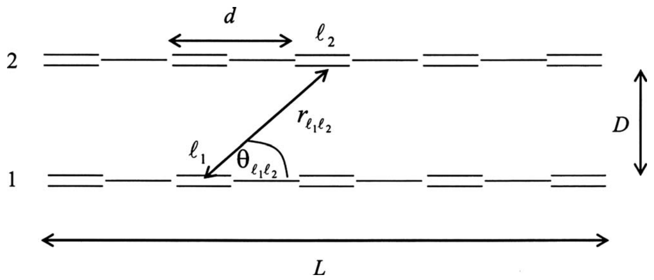

FIG. 1. The geometry of two conjugated polymers. D is the transverse separation. Also shown are the definitions of d, L, and θ.

$$E_W = -\sum_{A' \neq A} \frac{|V_{AA'}|^2}{\Delta E_1 + \Delta E_2}, \tag{4}$$

where $|A'\rangle$ is the excited state product,

$$|A'\rangle = |\mathrm{EX}\rangle_1 |\mathrm{EX}\rangle_2, \tag{5}$$

and $|\mathrm{EX}\rangle_m$ and ΔE_m represent an excited state and transition energy of polymer m, respectively. The matrix element $V_{AA'}$, defined as[13]

$$\begin{aligned} V_{A'A} &= \langle A'|\hat{V}|A\rangle \\ &= \sum_{i\in 1, j \in 2} V_{ij} [{}_1\langle \mathrm{GS}|(\hat{N}_i - 1)|\mathrm{EX}\rangle_1][{}_2\langle \mathrm{EX}|(\hat{N}_j - 1)|\mathrm{GS}\rangle_2], \end{aligned} \tag{6}$$

is formally the exciton transfer integral between both chains. V_{ij} is the Coulomb interaction between electrons in orbitals ϕ_i and ϕ_j, and $\hat{N}_i$ is the number operator for electrons in orbital ϕ_i. When $|\mathbf{r}_i - \mathbf{r}_j|$ is large compared to the interatomic spacing the Coulomb potential is

$$V_{ij} = \frac{q^2}{4\pi\epsilon_0\epsilon|\mathbf{r}_i - \mathbf{r}_j|}, \tag{7}$$

where $\mathbf{r}_i$ is the coordinate of atom i.

As shown in Ref. 6, for polymer chains whose separation exceeds their monomer size, d, the exciton transfer integral can be expressed as

$$V_{AA'} = \mu_{n_1}^{(1)} \mu_{n_2}^{(2)} \sum_{l_1 \in 1} \sum_{l_2 \in 2} \Psi_{\beta_1}(R_{l_1}) \frac{\kappa_{l_1 l_2}}{4\pi\epsilon_0 \epsilon r_{l_1 l_2}^3} \Psi_{\beta_2}(R_{l_2}), \tag{8}$$

where

$$\mu_n = \left(\frac{dq}{2\sqrt{2}}\right)\psi_n(0) \tag{9}$$

is the monomeric transition dipole moment, $r_{l_1 l_2}$ is the separation between the monomers l_1 and l_2, and $\kappa_{l_1 l_2} = (1 - 3\cos^2\theta_{l_1 l_2})$ is an orientational factor, as defined in Fig. 1. Here, indices 1 and 2 refer to polymer chains 1 and 2, respectively. $\psi_n(r)$ is the relative wavefunction of the exciton, labeled by the principle quantum number, n, and r is the relative coordinate. $\Psi_\beta(R)$ is the exciton center-of-mass wavefunction labeled by the pseudomomentum, β, and R is the center-of-mass coordinate.[14,15] For linear polymers with N equivalent monomers and open boundary conditions the exciton center-of-mass wavefunction satisfies

$$\Psi(R_l) = \sqrt{\frac{2}{N+1}} \sin(\beta R_l), \tag{10}$$

where $\beta = \pi j/(N+1)$ with $1 \leq j \leq N$.

An analytical expression was developed for $V_{AA'}$ in Ref. 6, where it was shown (assuming a plane-wave expansion for the center-of-mass wavefunction, Ψ) that

$$V_{AA'} \sim \left(\frac{1}{DL}\right)\left(1 - \frac{D}{\sqrt{(L^2 + D^2)}}\right), \tag{11}$$

and therefore $V_{AA'} \sim L/D^3$ for $L \ll D$, while $V_{AA'} \sim 1/LD$ for $L \gg D$. Thus, the condition required for the perturbation theory to be valid, namely, that $V_{AA'} \ll (\Delta E_1 + \Delta E_2)$, remains valid in the asymptotic limits. We also note that the crossover in scaling for $V_{AA'}$ as a function of L/D implies a crossover in scaling for E_W.

Identifying the excited state $|\mathrm{EX}\rangle$ with the quantum numbers n and β, the correction to the groundstate energy is thus

$$E_W = -\left(\frac{q^2 d^2}{8}\right) \sum_{n_1,\beta_1} \sum_{n_2,\beta_2} \times \frac{\left(\psi_{n_1}(0)\psi_{n2}(0) \sum_{l_1 \in 1} \sum_{l_2 \in 2} \Psi_{\beta_1}(R_{l_1}) \frac{\kappa_{l_1 l_2}}{4\pi\epsilon_0\epsilon r_{l_1 l_2}^3} \Psi_{\beta_2}(R_{l_2})\right)^2}{\Delta E(n_1,\beta_1) + \Delta E(n_2,\beta_2)}. \tag{12}$$

To proceed further with the computation of Eq. (12) we need to evaluate the exciton wavefunction, $\psi_n(r)$, and the transition energy, ΔE, for particular molecular systems with the appropriate Hamiltonian. We model the system by the semiempirical Pariser-Parr-Pople Hamiltonian, with parameters chosen to accurately model conjugated polymers. The Pariser-Parr-Pople model is

$$\begin{aligned} H = &-\sum_{i\sigma} t_i (c_{i\sigma}^\dagger c_{i+1\sigma} + c_{i+1\sigma}^\dagger c_{i\sigma}) \\ &+ U \sum_i \left(\hat{N}_{i\uparrow} - \frac{1}{2}\right)\left(\hat{N}_{i\downarrow} - \frac{1}{2}\right) + \frac{1}{2}\sum_{i \neq j} V_{ij}(\hat{N}_i - 1)(\hat{N}_j - 1), \end{aligned} \tag{13}$$

where $t_i = t(1 + (-1)^i \delta)$ is the hybridization integral, δ is the bond dimerization parameter, and $U = V(r_{ij} \to 0)$.

In the weak-coupling limit, defined by $U \ll 4t$, the excitations of this Hamiltonian are Mott-Wannier excitons described by the relevant exciton Schrödinger equation.[14,15] It is convenient to introduce this exciton Schrödinger equation in the effective mass (or continuum) limit, and to rescale energies by the effective Rydberg, E_I, and lengths by the effective Bohr length, a_0. This procedure is described in the Appendix. Taking $d = 2.8$ Å, $\delta = 0.1$, $t = 2.5$ eV, and $\epsilon = 2.25$ implies that $E_I = 0.58$ eV and $a_0 = 5.51$ Å. The low-lying exciton wavefunctions and energies are shown in Fig. 7 and Table I for these parameters.

Now, scaling energies by the effective Rydberg, E_I, and lengths by the monomer length, d, Eq. (12) becomes

TABLE I. The excitation energies for the lowest member of each of the lowest four exciton families in units of E_I using the parameter set $d=2.8$ Å, $\delta=0.1$, $t=2.5$ eV, and $\epsilon=2.25$, implying that $E_I=0.58$ eV and $a_0=5.51$ Å.

Exciton, n	Excitation energy, $\Delta E'(n)$
1	3.157
2	4.711
3	5.133
4	5.220

$$E'_W = -\left(\frac{1}{16a'}\right)^2 \sum_{n_1,\beta_1}\sum_{n_2,\beta_2} \times \frac{\left(\psi'_{n_1}(0)\psi'_{n_2}(0)\sum_{l_1\in 1}\sum_{l_2\in 2}\Psi_{\beta_1}(R_{l_1})\frac{\kappa_{l_1l_2}}{(r'_{l_1l_2})^3}\Psi_{\beta_2}(R_{l_2})\right)^2}{\Delta E'(n_1,\beta_1)+\Delta E'(n_2,\beta_2)}, \qquad (14)$$

where $a'=d/a_0$, $r'=r/d$, and E' represents an energy scaled by E_I. $\psi'=\psi/\sqrt{a'}$ to account for the change of normalization arising from the change of scale from that used in the Appendix in the definition of ψ.

We first establish the convergence of Eq. (14) with respect to the number of exciton families included in the summation. Figure 2 shows the computed E'_W versus n^{-1}, where n is the cumulative sum of all exciton families up to an including n. Extrapolating to $n^{-1}\rightarrow 0$ indicates that retaining just the first exciton family, $n=1$, gives results within 10% of the converged value.

Retaining just the $n=1$ exciton family, we now investigate the scaling of E'_W versus L and D. Figures 3 and 4 show E'_W versus D for fixed L. In the limit $L \ll D$, $E'_W \sim D^{-6}$, whereas in the limit $L \gg D$, $E'_W \sim D^{-5}$. Figures 5 and 6 show E'_W versus L for fixed D. In the limit $L \ll D$, $E'_W \sim L^2$, whereas in the limit $L \gg D$, $E'_W \sim L$. The scaling limits for $L \ll D$ conform to the point-dipole London prediction, Eq. (1), whereas those for $L \gg D$ satisfy the correct thermodynamic properties, as discussed in Sec. I. In the next section these scaling results are justified by a semiclassical derivation of the dispersion interaction using the line-dipole approximation.

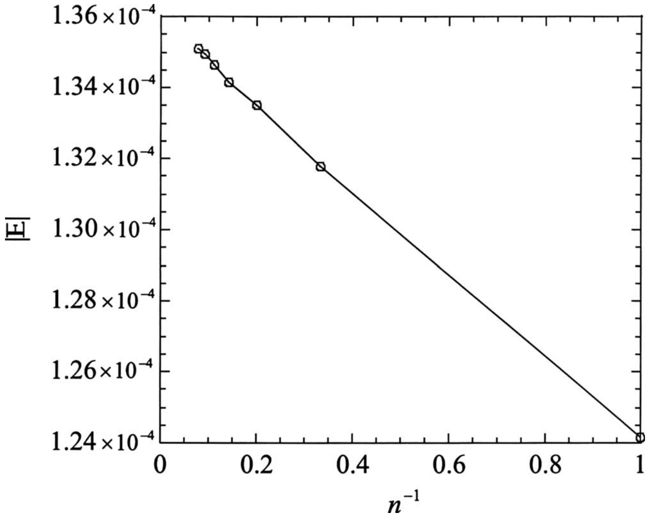

FIG. 2. The groundstate dispersion interaction, $|E_W|$ (in units of E_I $=0.58$ eV), vs n^{-1}, where n is the number of exciton families retained in the calculation. $D=5d$, $L=200d$, and $d=2.8$ Å.

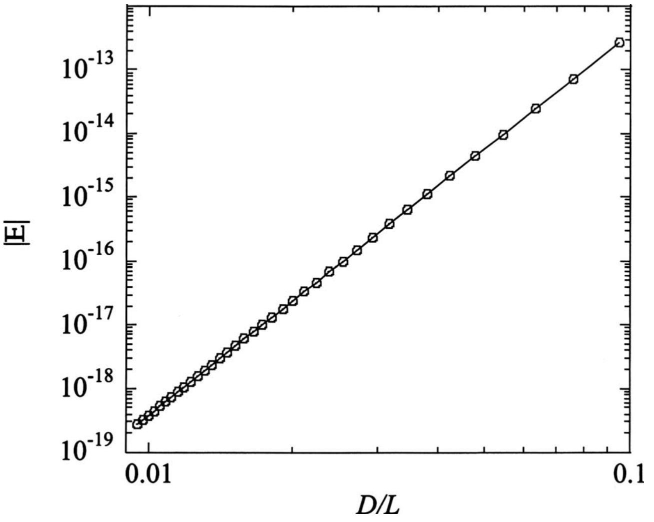

FIG. 3. The scaling relation for $|E_W|$ (in units of $E_I=0.58$ eV) vs D (in units of $d=2.8$ Å) in the limit $L \ll D$. L is fixed at $200d$. E_W is found to scale as D^{-6}.

III. DISTRIBUTED DIPOLE MODEL OF VAN DER WAALS INTERACTIONS

The scaling dependence of the groundstate interaction, E_W, on both the chain length, L, and the chain separation, D, can be determined semiclassically via the distributed dipole approximation without any assumptions of pairwise additive interactions.

The distributed (or line-dipole) approximation, which becomes essentially exact for $D \gtrsim 3d$, states that the transition dipole moment for a chain of N repeat units is[6,11,12]

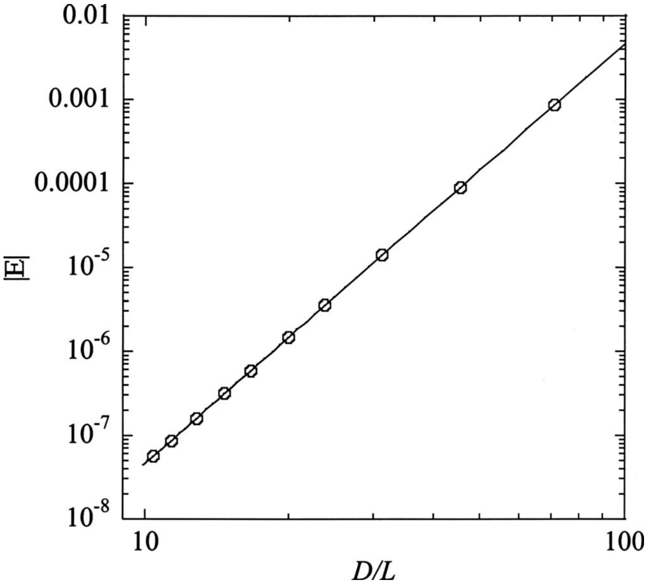

FIG. 4. The scaling relation for $|E_W|$ (in units of $E_I=0.58$ eV) vs D (in units of $d=2.8$ Å) in the limit $L \gg D$. L is fixed at $2000d$. E_W is found to scale as D^{-5}.

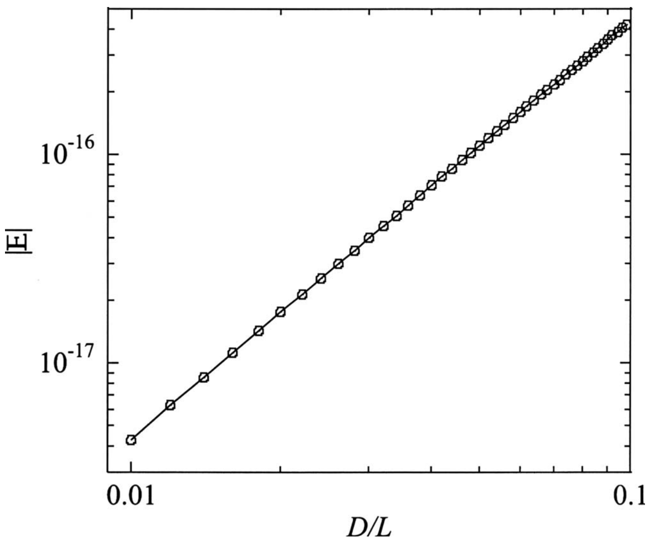

FIG. 5. The scaling relation of $|E_W|$ (in units of E_I=0.58 eV) vs L (in units of d=2.8 Å) in the limit $L \ll D$. D is fixed at 2000d. E_W is found to scale as L^2.

$$\mu_N = \sum_{l=1}^{N} \mu_l, \tag{15}$$

where μ_l is the transition dipole moment for the lth repeat unit,[6]

$$\mu_l = \mu \Psi(R_l), \tag{16}$$

μ is the monomeric transition dipole moment, as defined in Eq. (9), and $\Psi(R_l)$ is the exciton center-of-mass wavefunction.

Suppose that chain 1 undergoes a spontaneous fluctuation such that the instantaneous transition dipole is $\mu_N^{(1)}$. Then its subdipole on the l_1th repeat unit of chain 1 is thus

$$\mu_{l_1}^{(1)} = \mu^{(1)} \Psi(R_{l_1}). \tag{17}$$

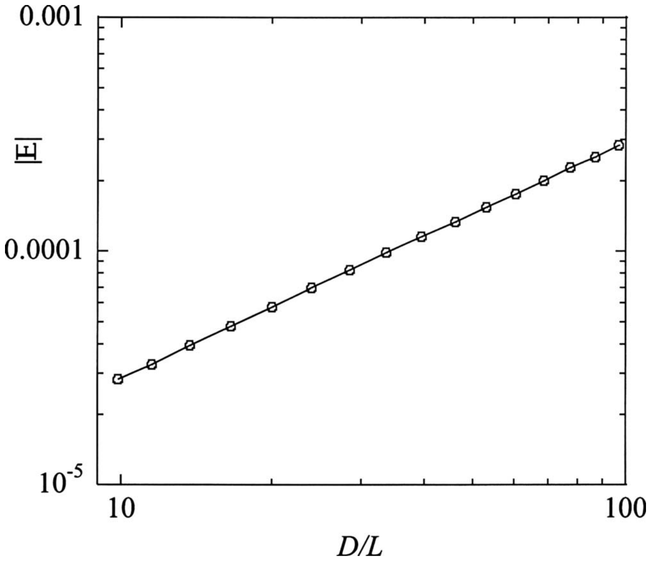

FIG. 6. The scaling relation for $|E_W|$ (in units of E_I=0.58 eV) vs L (in units of d=2.8 Å) in the limit $L \gg D$. D is fixed at 20d. E_W is found to scale as L.

This subdipole creates a longitudinal electric field, $E_z^{l_1 l_2}$, at the l_2th monomer on chain 2,

$$E_z^{l_1 l_2} = \mu_{l_1}^{(1)} \frac{(3\cos^2\theta_{l_1 l_2} - 1)}{4\pi\epsilon_0 \epsilon r_{l_1 l_2}^3}. \tag{18}$$

The total longitudinal electric field, $E_z^{l_2}$, at the l_2th monomer on chain 2 arising from all the monomers on chain 1,

$$E_z^{l_2} = \sum_{l_1 \in 1} E_z^{l_1 l_2}, \tag{19}$$

induces a subdipole on the l_2th monomer on chain 2,

$$\mu_{l_2}^{(2)} = \alpha E_z^{l_2}, \tag{20}$$

where α is the polarizability of the monomer, and is *independent* of chain length.

The induced dipoles on chain 2 cause an interaction between the two chains in two ways. First, there is the direct interaction between the subdipoles on chain 1 and those on chain 2,

$$E_W^{(1)} = \sum_{l_1 \in 1, l_2 \in 2} V_{l_1 l_2}, \tag{21}$$

where

$$V_{l_1 l_2} = -\mu_{l_1}^{(1)} \mu_{l_2}^{(2)} \frac{(3\cos^2\theta_{l_1 l_2} - 1)}{4\pi\epsilon_0 \epsilon r_{l_1 l_2}^3}. \tag{22}$$

Thus,

$$\begin{aligned} E_W^{(1)} &= -\alpha \sum_{l_1 \in 1, l_1' \in 1} \mu_{l_1}^{(1)} \mu_{l_1'}^{(1)} \sum_{l_2 \in 2} \\ &\quad \times \frac{(3\cos^2\theta_{l_1 l_2} - 1)}{4\pi\epsilon_0 \epsilon r_{l_1 l_2}^3} \frac{(3\cos^2\theta_{l_1' l_2} - 1)}{4\pi\epsilon_0 \epsilon r_{l_1' l_2}^3} \\ &= -\sum_{l_1 \in 1, l_1' \in 1} \mu_{l_1}^{(1)} \tilde{U}_{l_1 l_1'} \mu_{l_1'}^{(1)}, \end{aligned} \tag{23}$$

where

$$\tilde{U}_{l_1 l_1'} = \alpha \sum_{l_2 \in 2} \frac{(3\cos^2\theta_{l_1 l_2} - 1)}{4\pi\epsilon_0 \epsilon r_{l_1 l_2}^3} \frac{(3\cos^2\theta_{l_1' l_2} - 1)}{4\pi\epsilon_0 \epsilon r_{l_1' l_2}^3} \tag{24}$$

is the effective interaction between the subdipoles $\mu_{l_1}^{(1)}$ and $\mu_{l_1'}^{(1)}$ on chain 1 mediated by $\mu_{l_2}^{(2)}$ on the opposite chain.

Second, the subdipoles induced on chain 2 by the subdipoles of chain 1 interact between themselves causing an effective interaction between the chains,

$$E_W^{(2)} = \frac{1}{2} \sum_{l_2 \in 2, l_2' \in 2} V_{l_2 l_2'}, \tag{25}$$

where

$$V_{l_2 l'_2} = \frac{2\mu^{(2)}_{l_2}\mu^{(2)}_{l'_2}}{4\pi\epsilon_0\epsilon r^3_{l_2 l'_2}}. \tag{26}$$

Thus,

$$E^{(2)}_W = -\alpha^2 \sum_{l_2\in 2, l'_2\in 2} \frac{1}{4\pi\epsilon_0\epsilon r^3_{l_2 l'_2}} \times \sum_{l_1\in 1} \mu^{(1)}_{l_1} \frac{(3\cos^2\theta_{l_1 l_2} - 1)}{4\pi\epsilon_0\epsilon r^3_{l_1 l_2}} \times \sum_{l'_1\in 1} \mu^{(1)}_{l'_1} \frac{(3\cos^2\theta_{l'_1 l'_2} - 1)}{4\pi\epsilon_0\epsilon r^3_{l'_1 l'_2}}. \tag{27}$$

Assuming a plane-wave approximation for the center-of-mass wavefunction, namely, that $\Psi(R_l) \sim 1/\sqrt{L}$ implying that $\mu_l \sim \mu/\sqrt{L}$, allows Eq. (23) to be integrated analytically to give

$$E^{(1)}_W = -\frac{\alpha}{(4\pi\epsilon_0\epsilon)^2}\left(\frac{4(L^4 - 3D^2L^2 - 4D^4)}{LD(L^2+D^2)^{1/2}(L^2+4D^2)^2} + \frac{\tan^{-1}(L/D)}{8D^3} - \frac{L}{2(L^2+D^2)}\right). \tag{28}$$

For $L \ll D$, $E^{(1)}_W \to L^2/D^6$, whereas for $L \gg D$, $E^{(1)}_W \to 1/LD^3$. Equation (27) cannot be evaluated analytically. However, anumerical integration indicates that for $L \ll D$, $E^{(2)}_W \to (L/D)^{\nu(L)}(1/D^4)$ with $\nu(L) > 2$, whereas for $L \gg D$, $E^{(2)}_W \to L/D^5$.

Thus, for $L \ll D$, $E^{(1)}_W$ dominates and $E_W = E^{(1)}_W + E^{(2)}_W \to L^2/D^6$, while for $L \gg D$, $E^{(2)}_W$ dominates and $E_W \to L/D^5$. The semiclassical result is therefore in agreement with the quantum mechanical calculation presented in the previous section. We also note that although this result has the same asymptotic predictions as the pairwise additive expression shown in Eq. (2),[7] no such assumption about pairwise additive interactions has been made here.

IV. CONCLUDING REMARKS

In conclusion, the line-dipole approximation has been used to investigate the scaling of the groundstate dispersion interaction, E_W, between conjugated polymers of length L and transverse separation D. Both a second-order perturbation theory calculation using the Mott-Wannier exciton model of excited states and a semiclassical analysis of distributed dipoles indicate that at $L \sim D$ there is a crossover from the point-dipole approximation of $E_W \sim L^2/D^6$ for $L \ll D$ to the thermodynamically expected result of $E_W \sim L/D^5$ for $L \gg D$. We note that for $L \gg D$, $E_W \sim (D/L)E_L$, where $E_L \sim L^2/D^6$ is the London expression for the dispersion interaction. Thus, (up to numerical coefficients) the correct dispersion interaction is smaller than the London prediction in this limit.

The London expression for the dispersion interaction has been used to interpret spectral diffusion in conjugated polymer chains.[16,17] It would be informative to reexamine this analysis in the light of the present work. It would also be instructive to investigate the scaling dependence of the excited state screening energy as a function of D using a similar perturbation theory analysis with the Mott-Wannier exciton model. Soos *et al.*[18] have shown using a model of correlated electrons that the screening energy scales as D^{-3} for $L \gg D$. Finally, the role of retardation effects—which become important for dispersion interactions when conjugated segments are separated by distances comparable to the wavelength of light—also needs to be investigated in the context of the current work.

ACKNOWLEDGMENTS

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APPENDIX: EXCITON SCHRÖDINGER EQUATION

The exciton Schrödinger equation for Mott-Wannier excitons, derived from the Pariser-Parr-Pople model, was introduced in Refs. 14 and 15. In making the connection to the effective mass (or continuum) limit it is convenient to define the reduced mass as $\mu = \hbar^2/2t(1-\delta)d$, where d is the monomer size. Then, scaling lengths by the effective Bohr radius,

$$a_0(\beta) = \frac{4\pi\epsilon_0\epsilon\hbar^2\cos(\beta d/2)}{\mu e^2} \tag{A1}$$

and the energy by the effective Rydberg,

$$E_I(\beta) = \frac{\mu e^4}{2\hbar^2\cos(\beta d/2)(4\pi\epsilon_0\epsilon)^2}, \tag{A2}$$

the exciton Schrödinger equation becomes

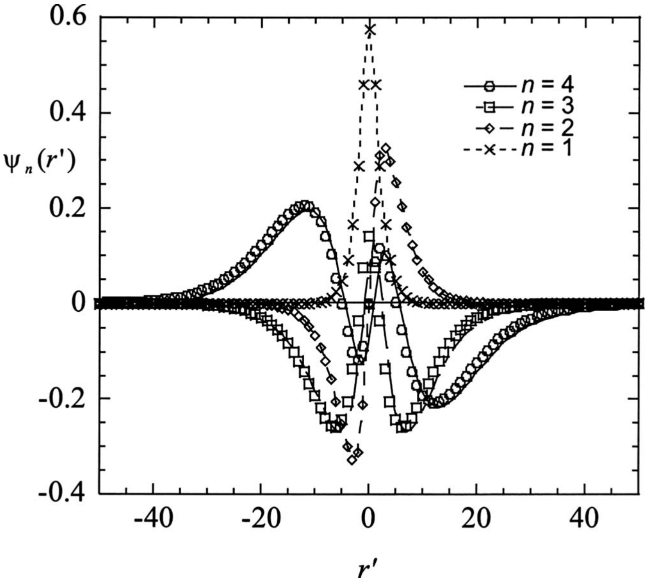

FIG. 7. The exciton wavefunction, ψ, derived from the exciton Schrödinger equation, Eq. (A3), using the parameter set $d=2.8$ Å, $\delta=0.1$, $t=2.5$ eV, and $\epsilon=2.25$, implying that $E_I=0.58$ eV and $a_0=5.51$ Å.

$$-\frac{1}{a'^2}(\psi_n(r'+a')+\psi_n(r'-a'))-\frac{2\psi_n(r')}{a'(1+r'^2)^{1/2}}$$
$$=E'_n\psi_n(r'), \tag{A3}$$

where $r'=r/a_0(\beta)$, $a'=d/a_0(\beta)$, $E'_n=E_n/E_I(\beta)$, and $\Delta'=t(1+\delta)/E_I(\beta)$.

The excitation energy relative to the groundstate energy is given by

$$\Delta E'_n=E'_n+\widetilde{U}'+2\Delta', \tag{A4}$$

where (E'_n+2/a'^2) is the exciton binding energy relative to the electron-hole continuum and

$$\widetilde{U}'=\frac{1}{a'}\left(1+\frac{1}{(1+(1/2)^2)^{1/2}}\right), \tag{A5}$$

using the Ohno form for the Coulomb interaction, which remains finite as $r'\rightarrow 0$.

The low-lying excitations are listed in Table I and plotted in Fig. 7 for the parameter set d=2.8 Å, δ=0.1, t=2.5 eV, and ϵ=2.25, implying that E_I=0.58 eV and a_0=5.51 Å.

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