

Many-body Green's-function calculations on the electronic excited states of extended systems

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Electron correlation corrections to the excitation energy of the lowest-lying singlet exciton state of polyethylene are evaluated with the aid of the quasiparticle energies obtained from second-order many-body perturbation theory and from the second-order inverse Dyson equation. A simple approximation is proposed to avoid the evaluation of the quasiparticle energies for high- and low-lying energy bands, which is particularly problematic in extended-system calculations. The inclusion of both the electron correlation effects and diffuse basis functions is important for the proper description of the exciton state. The electron correlation corrections calculated by this method appear to be too large, probably due to the neglect of the screening effects of the quasiparticle interactions. © 2000 American Institute of Physics. [S0021-9606(00)31017-0]

I. INTRODUCTION

There are two extremal approximations to the excited-state theory of extended systems—one in which electrons are treated nearly free and one in which they are treated as tightly bound to the individual units constituting the systems.¹ The low-lying excited states of many insulators with large band gaps do not fall into either of these categories, and are considered in-between these two extremal cases.^{2,3} As such, the electronic transitions associated with these excited states cannot be described appropriately either as band-to-band transitions or as excitations within the individual units; but, they should be handled by the theories that allow excited-state configurations of the interacting units to mix. Configuration interaction singles (CIS) and time-dependent Hartree–Fock (TDHF, also known as random phase approximation, RPA) theories are among the simplest such theories that can provide the zeroth-order descriptions of these excited states. We have recently applied these theories to the lowest-lying exciton state of all-*trans* polyethylene.⁴ The exciton binding energies calculated by these theories with the 6-31G* basis set were, however, not more than 50% of the experimental findings, and accordingly the calculated excitation energies were excessively higher than the experimental values. Experimentally, the threshold of photoemission of polyethylene (8.8 eV), which corresponds to the first ionization potential, occurs at a higher energy than the position of the optical absorption band edge (7.6 eV), which is associated with the lowest-lying singlet exciton state.^{5–9} Neither the CIS or TDHF method (with the 6-31G* basis set) can reproduce the correct order of these physical quantities; they predict the first ionization potential, which in these models is equivalent to the negative of the highest occupied orbital energy,¹⁰ to be lower than the excitation energy of the lowest-lying singlet exciton state.⁴ These results indicate that the inclusion of dynamical electron cor-

relation effects and, potentially, the use of an even larger basis set is warranted to obtain the excitation energies of polyethylene with reasonable accuracy.

In this study, we attempt to rectify these errors by including electron correlation effects in the excitation energies and in the ionization potentials with the aid of many-body Green's-function theory.^{11,12} The same approach was taken earlier by Suhai,^{13,14} by Liegener and Ladik,^{15–17} and recently by Rohlfing and Louie^{18,19} for the excitation energies and by Sun and Bartlett²⁰ for the ionization potentials. The approach taken by Suhai and by Liegener and Ladik amounts to invoking the quasiparticle energies calculated by many-body perturbation theory in solving the Bethe–Salpeter equation for the two-particle Green's function. Rohlfing and Louie, on the other hand, based their calculations on the quasiparticle energies obtained from density functional theory with a local exchange–correlation functional. We choose to employ the quasiparticle energies²¹ calculated from second-order many-body perturbation theory [MBPT(2)] (Refs. 10, 17, 22, 23) and from the second-order inverse Dyson equation [Dyson(2)] (Refs. 10, 17). Many-body perturbation theory offers a systematic route to improve the quasiparticle energies.²⁴ It is, however, important to realize that the MBPT(2) quasiparticle energies are well-defined only for the energy bands near the Fermi level and they frequently diverge for high- and low-lying energy bands. Consequently, the original computational procedure proposed by Suhai and by Liegener and Ladik may not be applied straightforwardly to many extended systems; the excitation energies calculated with this procedure are frequently erroneous. The Dyson(2) quasiparticle energies do not, in principle, suffer from this divergence problem, but, in practice, it is very cumbersome and time consuming to make the quasiparticle energies converge for high- and low-lying energy bands. In this study, we propose an approximation to this method which amounts to substituting the CIS amplitude for the electron–hole amplitude of the Bethe–Salpeter equation. This method, which we may safely apply to the low-

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lying excitons of insulators with large band gaps, requires the quasiparticle energies of only the few highest occupied and lowest virtual energy bands and thereby avoids the divergence problem of the MBPT(2) quasiparticle energies and also reduces the overall computational costs significantly. We apply this method to the lowest-lying exciton state of polyethylene.

II. THEORY

We construct the exciton wave function $|1\rangle$ of an infinite one-dimensional lattice (polymer), which is accessible by a direct transition, in the form

$$|1\rangle = \sum_{a,i} \sum_{k_i}^{\text{BZ}} A_{ai[k_i]}^{\text{QP}} \hat{a}_{a[k_i]}^\dagger \hat{a}_{i[k_i]} |0\rangle, \quad (1)$$

where we designate the ground-state wave function by $|0\rangle$. The operator $\hat{a}_{a[k_i]}^\dagger$ creates a quasielectron with energy band a and wave vector k_i , while the operator $\hat{a}_{i[k_i]}$ annihilates a quasielectron (creates a quasihole) with energy band i and wave vector k_i . We denote the energy bands that are occupied in the ground state by i, j and those that are unoccupied in the ground state by a, b . The electron-hole amplitude $A_{ai[k_i]}^{\text{QP}}$ and the corresponding excitation energy ω are determined by solving the Bethe-Salpeter equation for the two-particle Green's function.^{11,12} Within the usual approximations, the equation reduces to the matrix eigenvalue problem of the form^{18,25,26}

$$(\epsilon_{a[k_i]}^{\text{QP}} - \epsilon_{i[k_i]}^{\text{QP}}) A_{ai[k_i]}^{\text{QP}} + \sum_{b,j} \sum_{k_j}^{\text{BZ}} \{ \kappa (a^{[k_i]i[k_i]} | j^{[k_j]b[k_j]}) - (a^{[k_i]b[k_j]} | W(\omega) | j^{[k_j]i[k_i]}) \} A_{bj[k_j]}^{\text{QP}} = \omega A_{ai[k_i]}^{\text{QP}}, \quad (2)$$

where $\kappa=2$ for singlet excitons and $\kappa=0$ for triplet excitons. The quasiparticle energies ϵ^{QP} employed in this work are obtained from the MBPT(2) or Dyson(2) methods (see below) and the corresponding quasiparticle orbitals are the canonical HF crystalline orbitals $\{ \psi_p^{[k_p]}(\mathbf{r}) \}$.

The interaction of a quasielectron and a quasihole is described as a sum of the unscreened exchange term and the screened Coulomb term in the curly bracket of Eq. (2). The unscreened exchange term is a regular two-electron integral defined by

$$(p^{[k_p]} q^{[k_q]} | r^{[k_r]} s^{[k_s]}) = \int \psi_p^{[k_p]*}(\mathbf{r}_1) \psi_q^{[k_q]}(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \psi_r^{[k_r]*}(\mathbf{r}_2) \times \psi_s^{[k_s]}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (3)$$

with the canonical HF crystalline orbitals being linear combinations of atomic orbitals,

$$\psi_p^{[k_p]}(\mathbf{r}) = \frac{1}{\sqrt{K}} \sum_{\mu} \sum_n C_{\mu p}^{[k_p]} \exp(ink_p R_t) \chi_{\mu}^{(n)}(\mathbf{r}). \quad (4)$$

Here, R_t is the translational period, K is the number of unit cells in the system (that approaches infinity), and the atomic orbital $\chi_{\mu}^{(n)}(\mathbf{r})$ is a real spatial function centered in unit cell n . The crystalline orbital coefficients $\{ C_{\mu p}^{[k_p]} \}$ are determined by solving the Hartree-Fock-Roothaan equation of crystalline orbital theory.^{27,28} The screened Coulomb term contains the interaction operator that depends on the excitation energy ω (see Refs. 15, 16, 18, 25). In this work, we simply approximate this term by a regular two-electron integral,^{14,25} namely,

$$(a^{[k_i]b[k_j]} | W(\omega) | j^{[k_j]i[k_i]}) \approx (a^{[k_i]b[k_j]} | j^{[k_j]i[k_i]}). \quad (5)$$

The quasiparticle energies used in Eq. (2) are computed by the MBPT(2) or Dyson(2) methods. Invoking the diagonal approximation to the irreducible self-energy part truncated at second order, the inverse Dyson equation reduces to^{10,17}

$$\epsilon_{p[k_p]}^{\text{Dyson(2)}} = \epsilon_{p[k_p]}^{\text{HF}} + \sum_j \sum_{a,b} \sum_{k_j, k_b}^{\text{BZ}} \frac{2|(p^{[k_p]} a^{[k_a]} | j^{[k_j]b[k_b]})|^2 - \Re[(p^{[k_p]} a^{[k_a]} | j^{[k_j]b[k_b]}) (p^{[k_p]} b^{[k_b]} | j^{[k_j]a^{[k_a]}})^*]}{\epsilon_{p[k_p]}^{\text{Dyson(2)}} + \epsilon_{j[k_j]}^{\text{HF}} - \epsilon_{a[k_a]}^{\text{HF}} - \epsilon_{b[k_b]}^{\text{HF}}} + \sum_{i,j} \sum_b \sum_{k_j, k_b}^{\text{BZ}} \frac{2|(i^{[k_i]p^{[k_p]}} | j^{[k_j]b[k_b]})|^2 - \Re[(i^{[k_i]p^{[k_p]}} | j^{[k_j]b[k_b]}) (i^{[k_i]b[k_b]} | j^{[k_j]p^{[k_p]}})^*]}{\epsilon_{p[k_p]}^{\text{Dyson(2)}} + \epsilon_{b[k_b]}^{\text{HF}} - \epsilon_{i[k_i]}^{\text{HF}} - \epsilon_{j[k_j]}^{\text{HF}}}, \quad (6)$$

with the wave vector indexes k_a and k_i being given for each set of (k_p, k_j, k_b) by the relation^{10,23,29}

$$k_p + k_j = k_a + k_b + \frac{2m\pi}{R_t}, \quad (7)$$

$$k_i + k_j = k_p + k_b + \frac{2n\pi}{R_t}, \quad (8)$$

where m and n are integers. Equation (6) has to be solved iteratively to find the Dyson(2) quasiparticle energies $\{ \epsilon_{p[k_p]}^{\text{Dyson(2)}} \}$. This can be accomplished straightforwardly if the root of the equation is sufficiently distant from all the singularities of the right-hand side of Eq. (6). This is generally the case with the quasiparticle energy bands near the Fermi level, but many of the roots that belong to high- and low-lying energy bands are embedded in the manifold of singularities. In principle, one can avoid false roots due to these

singularities and ensure convergence by introducing a complex damping factor in the denominators, which tends to zero at convergence. In practice, however, we find it increasingly cumbersome to obtain converged quasiparticle energies by

this procedure for high- and low-lying energy bands as the basis set and the number of wave vectors become larger.

Alternatively, one can employ the MBPT(2) quasiparticle energies^{10,22,23} which are calculated by

$$\begin{aligned} \epsilon_{p[k_p]}^{\text{MBPT}(2)} = & \epsilon_{p[k_p]}^{\text{HF}} + \sum_j \sum_{a,b} \sum_{k_j,k_b}^{\text{BZ}} \frac{2|(p^{[k_p]}a^{[k_a]}|j^{[k_j]}b^{[k_b]})|^2 - \Re[(p^{[k_p]}a^{[k_a]}|j^{[k_j]}b^{[k_b]}) (p^{[k_p]}b^{[k_b]}|j^{[k_j]}a^{[k_a]})*]}{\epsilon_{p[k_p]}^{\text{HF}} + \epsilon_{j[k_j]}^{\text{HF}} - \epsilon_{a[k_a]}^{\text{HF}} - \epsilon_{b[k_b]}^{\text{HF}}} \\ & + \sum_{i,j} \sum_b \sum_{k_j,k_b}^{\text{BZ}} \frac{2|(i^{[k_i]}p^{[k_p]}|j^{[k_j]}b^{[k_b]})|^2 - \Re[(i^{[k_i]}p^{[k_p]}|j^{[k_j]}b^{[k_b]}) (i^{[k_i]}b^{[k_b]}|j^{[k_j]}p^{[k_p]})*]}{\epsilon_{p[k_p]}^{\text{HF}} + \epsilon_{b[k_b]}^{\text{HF}} - \epsilon_{i[k_i]}^{\text{HF}} - \epsilon_{j[k_j]}^{\text{HF}}}, \end{aligned} \quad (9)$$

with k_a and k_i being given by Eq. (8). The evaluation of the MBPT(2) quasiparticle energies does not require an iterative procedure, and hence it can be carried out an order of magnitude faster than that of the Dyson(2) quasiparticle energies. However, the MBPT(2) quasiparticle energies are well-defined only when the corresponding HF orbital energies are in the energy range given by¹⁰

$$\epsilon_{\text{HOMO}}^{\text{HF}} - E_g^{\text{HF}} < \epsilon_{p[k_p]}^{\text{HF}} < \epsilon_{\text{LUMO}}^{\text{HF}} + E_g^{\text{HF}}, \quad (10)$$

where E_g^{HF} is the HF fundamental band gap. The MBPT(2) quasiparticle energies may diverge outside this energy range, and they are very frequently erroneous (in the sense that they do not form smooth energy band curves) for high- and low-lying energy bands.

It should be noted that the substitution of the HF orbital energies for the quasiparticle energies together with the approximation for the screened Coulomb term, Eq. (5), reduces Eq. (2) to the CIS equation for extended systems^{4,14,30}

$$\begin{aligned} (\epsilon_{a[k_i]}^{\text{HF}} - \epsilon_{i[k_i]}^{\text{HF}})A_{ai[k_i]}^{\text{HF}} + \sum_{b,j} \sum_{k_j}^{\text{BZ}} \{ \kappa(a^{[k_i]}i^{[k_i]}|j^{[k_j]}b^{[k_j]}) \\ - (a^{[k_i]}b^{[k_j]}|j^{[k_j]}i^{[k_i]}) \} A_{bj[k_j]}^{\text{HF}} = \omega A_{ai[k_i]}^{\text{HF}}. \end{aligned} \quad (11)$$

In this particular case, the total energy of an excited state is the expectation value of the Hamiltonian H , and the corresponding excitation energy ω can be expressed as

$$\begin{aligned} \omega = & \sum_{a,i} \sum_{k_i}^{\text{BZ}} |A_{ai[k_i]}^{\text{HF}}|^2 (\epsilon_{a[k_i]}^{\text{HF}} - \epsilon_{i[k_i]}^{\text{HF}}) \\ & + \sum_{a,i} \sum_{b,j} \sum_{k_i,k_j}^{\text{BZ}} A_{ai[k_i]}^{\text{HF}*} A_{bj[k_j]}^{\text{HF}} \{ \kappa(a^{[k_i]}i^{[k_i]}|j^{[k_j]}b^{[k_j]}) \\ & - (a^{[k_i]}b^{[k_j]}|j^{[k_j]}i^{[k_i]}) \}. \end{aligned} \quad (12)$$

For insulators with large band gaps, it is not unreasonable to expect the electron-hole amplitude $A_{ai[k_i]}^{\text{QP}}$ obtained from Eq. (2) to be close to $A_{ai[k_i]}^{\text{HF}}$ from Eq. (11). By approximating $A_{ai[k_i]}^{\text{QP}}$ by $A_{ai[k_i]}^{\text{HF}}$ and using the relation (12), we may write the electron correlation corrections to the excitation energies in a compact form as

$$\Delta\omega = \sum_{a,i} \sum_{k_i}^{\text{BZ}} |A_{ai[k_i]}^{\text{HF}}|^2 \{ (\epsilon_{a[k_i]}^{\text{QP}} - \epsilon_{i[k_i]}^{\text{QP}}) - (\epsilon_{a[k_i]}^{\text{HF}} - \epsilon_{i[k_i]}^{\text{HF}}) \}. \quad (13)$$

This expression suggests that we need to calculate the quasiparticle energies of only those orbitals that are associated with appreciably large absolute values of $A_{ai[k_i]}^{\text{HF}}$. The wave functions of the lowest-lying exciton states are generally linear combinations of configuration in which an electron is promoted from one of the few highest-lying occupied bands to one of the few lowest-lying virtual bands, and hence the contributions from the high- and low-lying energy bands to $\Delta\omega$ are negligible. This approximation, therefore, allows us to avoid the divergence problem of the MBPT(2) quasiparticle energies and the slow convergence of the Dyson(2) quasiparticle energies for high- and low-lying energy bands and also reduces the computational costs significantly. We shall show that the approximation reproduces the major part of the dynamical correlation effects on the excitation energies of the lowest-lying exciton state of polyethylene. It should be kept in mind, however, that the *ad hoc* assumption made here that $A_{ai[k_i]}^{\text{HF}}$ well approximates $A_{ai[k_i]}^{\text{QP}}$ may become less appropriate for systems with smaller band gaps, and Eq. (13) should not be applied for semiconductors with small band gaps.

III. RESULTS AND DISCUSSION

The method outlined above is implemented in the POLYMER program.³¹ The CIS calculations are carried out using Davidson's trial-vector algorithm³² with the atomic-orbital-based two-electron integrals evaluated by direct or disk-based algorithm. The details of the CIS implementation are given in Ref. 4. The methods for computing the MBPT(2) and Dyson(2) quasiparticle energies are implemented with a minor modification to the program for evaluating the MBPT(2) energies,²⁹ which uses the atomic-orbital-based two-electron integrals stored externally. We apply these methods to calculations of the total energy, the fundamental band gap, the energy of the highest occupied orbital, and the excitation energy to the lowest-lying singlet exciton state of polyethylene. The HF and CIS methods are carried out using basis sets from STO-3G, 3-21G, 6-31G, 6-31G*, 6-31(+)/G

TABLE I. Total energy per C_2H_4 unit (E), band gap (E_g), negative of the highest occupied orbital energy ($-\epsilon$), and vertical excitation energy to the lowest-lying singlet exciton state (ω) of an infinitely long all-*trans* polyethylene chain calculated by the HF and CIS methods within the frozen core approximation at the B3LYP/6-31G* optimized geometry (CC bond length: 1.5344 Å; CH bond length: 1.1005 Å; CCC bond angle: 113.60°; HCH bond angle: 105.94°). The values of the parameters (M, N, K) used in the HF and CIS calculations are: (6,14,18) for STO-3G, 3-21G, 6-31G, 6-31G*; (20,40,40) for 6-31(+)G and 6-31(+, +)G.

Basis set	E /hartree	E_g /eV	$-\epsilon$ /eV	ω /eV
STO-3G ^a	-77.159 644	23.81	9.72	15.89
3-21G ^a	-77.637 595	17.85	10.85	12.53
6-31G ^a	-78.036 449	16.88	10.84	11.70
6-31G* ^a	-78.068 976	17.02	10.92	11.77
6-31(+)G ^b	-78.036 869	13.55	10.87	9.85
6-31(+, +)G ^c	-78.037 116	12.30	10.91	9.17
Experiment ^d	...	8.8	8.8	7.6

^aSee also Ref. 4.

^bThe 6-31G basis set augmented with an s-type diffuse function ($\zeta=0.0438$) for carbon atom.

^cThe 6-31G basis set augmented with an s-type diffuse function ($\zeta=0.0438$) for carbon atom and an s-type diffuse function ($\zeta=0.0360$) for hydrogen atom.

^dThe photoconduction threshold (E_g), the photoemission threshold ($-\epsilon$), and the optical absorption band edge (ω) as reported in Refs. 5 and 7.

(the standard 6-31G basis set augmented with an s-type diffuse function for carbon), and 6-31(+, +)G (the standard 6-31G basis set augmented with an s-type diffuse function for carbon and an s-type diffuse function for hydrogen). The MBPT(2) and Dyson(2) calculations are performed with basis sets up to 6-31(+)G and 6-31G*, respectively. The 1s core energy bands are kept frozen in the CIS, MBPT(2), and Dyson(2) procedures. We employ the Namur cutoff criterion for the lattice summations;³³ we have computed the atomic-orbital-based two-electron integrals of the form $(\mu^{(0)} \nu^{(l)} | \lambda^{(m)} \kappa^{(n)})$ with the unit cell indexes in the range

$$-M < l < +M, \quad (14)$$

$$-N < m < +N, \quad (15)$$

$$m - M < n < m + M, \quad (16)$$

where M and N are the parameters defining the cutoff criterion. The values of the parameters M and N , as well as the number of evenly spaced wave vector sampling points K in the first Brillouin zone used in the calculations, are given in the tables.

The results of the CIS calculations are compiled in Table I. First, we note that the calculated excitation energies are consistently smaller than the corresponding fundamental band gaps,^{4,30} which results are consistent with the experimental findings that the optical absorption band edge of polyethylene does not accompany photoconduction, but is associated with an exciton transition. It should be noted that time-dependent density functional theory (TDDFT) employing popular local and gradient-corrected functionals yields excitation energies that coincide with the corresponding fundamental band gaps.⁴ Second, it may be noticed that the calculated excitation energies and fundamental band gaps depend significantly on the basis set. The calculated values of these quantities decrease by several electron volts upon in-

clusion of diffuse basis functions. This observation indicates that the lowest virtual orbital of polyethylene has large spatial spread and the lowest-lying singlet exciton state of polyethylene is of substantial Rydberg character. This is consistent with the fact that the lowest-lying singlet excited states of *n*-alkane molecules are Rydberg states. In contrast, the calculated energy of the highest occupied orbital converges rapidly with the size of the basis sets. The negative of this calculated value (10.9 eV) approximates the ionization potential of polyethylene by virtue of Koopmans' theorem, and it may be compared with the measured photoemission threshold (8.8 eV).

When the basis set does not contain diffuse basis functions, the HF and CIS calculations fail to reproduce the correct order of the photoemission threshold and the optical absorption band edge.⁴ The addition of diffuse basis functions rectifies this qualitative error. The negative of the highest occupied orbital energy (10.9 eV) and excitation energy (9.2 eV) calculated with the 6-31(+, +)G basis set are, however, substantially higher than the measured photoemission threshold (8.8 eV) and optical absorption band edge (7.6 eV), respectively. The deviation between the calculated and observed photoemission threshold (10.9–8.8=2.1 eV) is solely ascribed to the dynamical electron correlation effects (see below). The error between the calculated and observed excitation energies (9.2–7.6=1.6 eV) may be reduced slightly by further addition of diffuse basis functions, but we consider that the major part of the error is again ascribed to the dynamical electron correlation effects. This point is substantiated by calculations for *n*-alkane molecules using various diffuse basis sets performed with the Q-CHEM program package.³⁴ For example, the excitation energy of the lowest-lying singlet excited state of *n*-pentane (at the structure similar to the one we used for an infinite chain) calculated by the CIS method in conjunction with the 6-31G, 6-31(+)G, 6-31(+, +)G, 6-31(2+, 2+)G, and 6-31(2+, 2+)G** basis sets are 12.1, 10.1, 9.6, 9.4, and 9.4 eV, respectively. The excitation energies of pentane are consistently higher than the corresponding excitation energies of polyethylene by about 0.4 eV, and the results obtained from the 6-31(+, +)G and 6-31(2+, 2+)G** basis set do not differ from each other by more than a few tenths of an electron volt.

Fujihira and Inokuchi⁶ and Less and Wilson⁷ interpreted their experimental results as indicating that the fundamental band gap of polyethylene coincided with the ionization potential within a fraction of an electron volt. The calculated values of the fundamental band gap and the negative of the highest occupied orbital energy are significantly different from each other, apparently not supporting this interpretation. However, these calculated quantities exhibit different basis-set dependence, and it is not unreasonable to expect that these calculated quantities might converge to values which are close to each other at the basis set limit. Indeed, we observe that the calculated energy of the lowest virtual orbital approaches the vacuum level as we add diffuse basis functions to the basis set. The HF calculation on pentane using the 6-31(2+, 2+)G** basis set also indicates that the lowest virtual orbital lies higher in energy than the vacuum

TABLE II. Total energy per C_2H_4 unit (E), band gap (E_g), negative of the highest occupied orbital energy ($-\epsilon$), and vertical excitation energy to the lowest-lying singlet exciton state (ω) of an infinitely long all-*trans* polyethylene chain calculated by the CIS method using the MBPT(2) and Dyson(2) (given in the parentheses) quasiparticle energies within the frozen core approximation at the B3LYP/6-31G* optimized geometry (CC bond length: 1.5344 Å; CH bond length: 1.1005 Å; CCC bond angle: 113.60°; HCH bond angle: 105.94°). The excitation energies are obtained by employing the quasiparticle energies of the four highest occupied and four lowest virtual bands. The values of the parameters (M, N, K) used in the MBPT(2) and Dyson(2) calculations are: (9,9,9) for STO-3G, 3-21G, 6-31G, 6-31G*; (10,20,20) for 6-31(+)G.

Basis set	$E/\text{hartree}$	E_g/eV	$-\epsilon/\text{eV}$	ω/eV
STO-3G	-77.262 916	20.03 (20.29)	7.88 (8.01)	12.31 (12.57) ^a
3-21G	-77.820 970	14.48 (14.78)	8.64 (8.88)	9.17 (9.46)
6-31G	-78.219 773	13.40 (13.72)	8.44 (8.71)	8.22 (8.55)
6-31G*	-78.331 327	13.55 (13.88)	8.75 (9.02)	8.29 (8.63)
6-31(+)G ^b	-78.221 061	10.95	8.97	6.92
Experiment ^c	...	8.8	8.8	7.6

^aThe excitation energies obtained by the method originally proposed by Suhai taking into account the MBPT(2) and Dyson(2) quasiparticle energies of all the bands (excluding 1s core bands) are 12.06 and 12.33 eV, respectively.

^bThe 6-31G basis set augmented with an s-type diffuse function ($\zeta=0.0438$) for carbon atom.

^cThe photoconduction threshold (E_g), the photoemission threshold ($-\epsilon$), and the optical absorption band edge (ω) as reported in Refs. 5 and 7.

level by no more than 0.3 eV, while the excitation energy to the lowest singlet state is smaller by a few electron volts than either the fundamental band gap or the negative of the highest occupied orbital energy.

The results of the calculations using the MBPT(2) and Dyson(2) quasiparticle energies are given in Table II. The MBPT(2) and Dyson(2) calculations require large external storage for two-electron integrals, which limits the size of the basis sets that we can explore with these methods. It may be immediately noticed from the table that the results obtained from the Dyson(2) calculations exhibit parallel behavior to the corresponding results obtained from the MBPT(2) calculations. The fundamental band gaps, the negatives of the highest occupied orbital energy, and the excitation energies calculated from the Dyson(2) method are consistently larger than the MBPT(2) values by a few tenths of an electron volt. In the following, therefore, we confine our discussions to the results obtained from the MBPT(2) calculations. The conclusions drawn from the MBPT(2) results apply equally well to the Dyson(2) results.

The excitation energies obtained from the original procedure of Suhai^{13,14} using the MBPT(2)/STO-3G quasiparticle energies of all the energy bands (excluding the 1s core energy bands) is 12.06 eV. The approximate method outlined in the previous section yields the calculated excitation energy of 12.31 eV using the corresponding quasiparticle energies of only the four highest occupied and the four lowest virtual energy bands, which are in the range of Eq. (10). We consider that the approximation is reasonably good, since it accounts for 97% of the exciton binding energy predicted by the original procedure, with substantially reduced computational costs. It should be noted that the increase in the wave vector sampling points or the use of larger basis set renders

the original procedure ill-conditioned since some of the orbitals in the MBPT(2) quasiparticle energy bands inevitably cause zero or a near-zero denominator in Eq. (9).

The MBPT(2) quasiparticle energies of the highest occupied orbital converge rapidly while increasing the size of the basis sets. They reproduce the measured value of the photoemission threshold (8.8 eV) with quantitative accuracy.²⁰ The large deviation of 2.1 eV between the HF results and the experimental value is, therefore, ascribed to the dynamical electron correlation effects. The calculated fundamental energy gaps and excitation energies exhibit slower convergence with respect to the basis-set size. Upon inclusion of electron correlation effects in the orbital energies, occupied energy bands generally shift upward and virtual energy bands shift downward. The calculated fundamental energy gaps and excitation energies, therefore, undergo larger changes than the calculated highest occupied orbital energies, upon inclusion of the electron correlation effects within the present scheme, since the former values are dependent on the virtual orbital energies as well as on the occupied orbital energies while the latter depends only on the occupied orbital energies. As can be seen in the table, MBPT(2) corrects the CIS excitation energies toward the direction of experimental value, although the corrections appear to be too large; the excitation energy calculated with the 6-31(+)G basis set is 6.9 eV and is lower than the experimental value (7.6 eV). It can be inferred from Tables I and II that the use of larger basis sets containing two or more diffuse basis functions on carbon and hydrogen would lead to a further decrease in the MBPT(2) excitation energy, although such calculations are prohibitively expensive due to the necessity of taking enormously large truncation radii for the lattice summations in crystalline orbital calculations. It should be remembered that in the present study the quasidelectron-quasihole interaction, which will be a screened interaction and is expected to be weaker than the bare electron-hole interaction, is approximated by the bare Coulomb interaction, Eq. (5). Therefore, the decrease in the excitation energies upon inclusion of electron correlation effects might as well be exaggerated due to this particular approximation to the interaction.¹⁴⁻¹⁶ It may be said that the electron correlation effects on the excitation energy of polyethylene evaluated by MBPT(2) within the scheme presented here are substantially overestimated, probably due to the neglect of the screening effects of Coulomb interaction between quasidelectrons and quasiholes. The approximation, Eq. (13), is unlikely to be responsible for the overestimation of the electron correlation effects, since it reproduces reasonably well the excitation energy obtained from the original procedure with the STO-3G basis set.

IV. CONCLUSION

We point out that the Green's-function method proposed previously for computing excitation energies using the MBPT(2) quasiparticle energies is not necessarily applicable to extended systems, since the MBPT(2) quasiparticle energies are ill-defined for high- and low-lying energy bands. For insulators with large band gaps, the electron correlation corrections to the excitation energies obtained from this original

procedure are approximated reasonably well by the sum of the differences between the HF orbital energies and quasiparticle energies weighted by the square of the corresponding CIS amplitudes. This approximation requires the evaluation of quasiparticle energies of the orbitals that are associated with the appreciably large absolute values for the CIS amplitude. For the lowest-lying exciton states, these orbitals typically belong to the few highest occupied and lowest virtual energy bands, whose quasiparticle energies are normally well-defined. We find that this scheme reproduces the exciton binding energies predicted by the original approach within a few tenths of an electron volt for polyethylene.

The inclusion of diffuse basis functions significantly lowers the calculated excitation energies at the CIS level, indicating that the lowest-lying singlet exciton state of polyethylene has substantial Rydberg character. When combined with a diffuse basis set, the HF and CIS methods reproduce the correct order of the photoemission threshold and optical absorption band edge. The photoemission threshold and excitation energy calculated with the 6-31(+,+)G basis set are, however, higher than the corresponding experimental values by 2.1 and 1.6 eV, respectively. The latter deviation will be reduced slightly by the further inclusion of diffuse basis functions, but the major source of these deviations is considered to be the neglect of electron correlation effects. The MBPT(2) and Dyson(2) calculations reproduce the measured photoemission threshold remarkably well. The electron correlation effects of the excitation energies accounted for by these methods are, on the other hand, overestimated. We ascribe this to the neglect of screening effects of the interaction between the quasielectrons and quasiholes. We hope to include such effects in the calculated excitation energies in the future.

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