Convergence Behavior of Many-Body Perturbation Theory with Lattice Summations in Polymers

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The convergence behavior of many-body perturbation theory (MBPT) with lattice summations directly reflects the spatial property of electron correlation in extended systems. A knowledge of such properties is essential for both theory and numerical calculations. It is shown solely from theory that the second-order MBPT contribution to the total energy per unit cell in polymers converges with lattice size N as $1/N^3$ while the second-order MBPT contribution to the band energy converges as $1/N^2$. These convergence behaviors are demonstrated numerically for polyacetylene. [S0031-9007(97)05006-0]

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It is well known that the most interesting phenomena in crystals and polymers such as band gaps, optical and magnetic properties, superconductivity, etc., have not been well described theoretically [1,2] since electron correlation [3] is a key element in these phenomena. Currently the most widely used method in solid state applications is density functional theory (DFT) [4,5], which can approximately include electron correlation but fails for many problems. Furthermore, there is no systematic way to improve DFT results. To the contrary, many-body perturbation-theory [6] (MBPT), coupled cluster theory [7–9] and many-body green function or propagator methods [10] offer approaches for correlation corrections that are systematically improvable [11–15]. We have recently demonstrated that second-order MBPT [MBPT(2)] can provide the essential electron correlation effects for occupied bands to accurately explain the photoelectron spectra (x-ray photoemission spectroscopy and ultraviolet photoemission spectroscopy) for polyethylene [16] and the vibrational spectra of polymethineimine [17]

Unlike the case for finite molecules, for periodic, infinite systems, there are many lattice summations which necessarily go to infinity. Some of these infinite summations may introduce divergences or a singularity [18]. Most recently, it has been shown that the divergence will vanish either by the cancellation of the divergent diagrams which always appear in pairs [19,20], or by integration over the reciprocal space [19]. However, nothing more is known about the general convergence behavior, yet it reflects the spatial property of the electron correlation and, once known, can be used to obtain fully converged numerical results.

In this Letter, we will derive the convergence behavior with lattice size, the cutoff of the lattice summations, of the largest correlation correction, MBPT(2), for the total energy per unit cell, $E_{\mathrm{uc}}^{(2)}$, and for the band energy, $\epsilon_P^{(2)}$. Numerical results show that they are quite different [15]. Using a multipole expansion and Wannier orbitals, we will show explicitly that $E_{\mathrm{uc}}^{(2)}$ converges as $1/N^3$ with the lattice summation cutoff N while $\epsilon_P^{(2)}$ converges a power slower as $1/N^2$, when N is larger than N_0, the size of the best localized Wannier orbitals [21] for the system. The slower convergence behavior of $\epsilon_P^{(2)}$ is due to the "dipole-Coulomb" interaction which vanishes in $E_{\mathrm{uc}}^{(2)}$. The convergence behavior will also be demonstrated by numerical MBPT(2) results for polyacetylene.

With translation symmetry, the one-electron spatial orbital wave functions in a periodic extended system can be written as Bloch functions,

$$\phi_{p\mathbf{k}_p}(\mathbf{r}) = \frac{1}{\sqrt{\mathcal{N}}} \sum_{\mathbf{R}_l} e^{i\mathbf{k}_p\cdot\mathbf{R}_l}\omega_p(\mathbf{r}-\mathbf{R}_l), \tag{1}$$

where $\mathcal{N}$ is the total number of unit cells approaching ∞ and $\omega_p(\mathbf{r}-\mathbf{R}_l)$ are Wannier functions which can be expressed as summations of the atomic orbitals. With a proper choice of phase factors for Bloch orbitals, Wannier functions can be localized into a few unit cells in insulators or semiconductors [2,12]. Wannier functions are orthonormal functions, e.g.,

$$\langle\omega_p(\mathbf{r}-\mathbf{R}_l)|\omega_{p'}(\mathbf{r}-\mathbf{R}_{l'})\rangle = \delta_{pp'}\delta_{ll'}\,. \tag{2}$$

The two-electron integrals over the Bloch functions can be expressed as [15,19]

$$\langle(p\mathbf{k}_p)(q\mathbf{k}_q)|(r\mathbf{k}_r)(s\mathbf{k}_s)\rangle = \delta_{\mathbf{k}_q,\mathbf{T}(\mathbf{k}_r+\mathbf{k}_s-\mathbf{k}_p)}G(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)/\mathcal{N}\,, \tag{3}$$

where

$$\begin{aligned} G(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s) = \sum_{\mathbf{R}_{l'}\mathbf{R}_l,\mathbf{R}_{l''}} & e^{i[\mathbf{k}_r\cdot\mathbf{R}_{l'}-(\mathbf{k}_r-\mathbf{k}_p)\cdot\mathbf{R}_l+\mathbf{k}_s\cdot\mathbf{R}_{l''}]} \\ & \times\langle\omega_p(\mathbf{r}_1)\omega_q(\mathbf{r}_2-\mathbf{R}_l)|r_{12}^{-1}|\omega_r(\mathbf{r}_1-\mathbf{R}_{l'})\omega_s(\mathbf{r}_2-\mathbf{R}_l-\mathbf{R}_{l''})\rangle\,. \end{aligned} \tag{4}$$

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It is easy to see that $G(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)$ converges exponentially with $\mathbf{R}_{l'}$ and $\mathbf{R}_{l''}$ while it has a much slower convergence with $\mathbf{R}_l$. The convergence behavior of MBPT with lattice summations is mainly determined by $\mathbf{R}_l$. In the following, we assume that convergence with respect to both $\mathbf{R}_{l'}$ and $\mathbf{R}_{l''}$ has already been reached and we use the lattice size to indicate the cutoff for the summation over $\mathbf{R}_l$.

Since Wannier orbitals are localized for insulators and semiconductors, we can always find a N_0 such that the radius of the Wannier orbitals for a given system are all smaller than R_{N_0}. Using V to denote the lattice space region defined by R_{N_0}, Eq. (4) can then be further expressed as

$$G(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s) = G_0(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s) + G_1(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)\,, \qquad (5)$$

where

$$G_0(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s) = \sum_{\mathbf{R}_l\in \mathrm{V}}\sum_{\mathbf{R}_{l'},\mathbf{R}_{l''}} e^{i[\mathbf{k}_r\cdot\mathbf{R}_{l'}-(\mathbf{k}_r-\mathbf{k}_p)\cdot\mathbf{R}_l+\mathbf{k}_s\cdot\mathbf{R}_{l''}]} \times \langle\omega_p(\mathbf{r}_1)\omega_q(\mathbf{r}_2-\mathbf{R}_l)\,|r_{12}^{-1}|\omega_r(\mathbf{r}_1-\mathbf{R}_{l'})\omega_s(\mathbf{r}_2-\mathbf{R}_l-\mathbf{R}_{l''})\rangle \qquad (6)$$

can be calculated exactly. The convergence property of $G(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)$ with lattice summations is now totally determined by that of $G_1(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)$. Using a Taylor expansion for $r_{12}^{-1} = |\mathbf{R}_l - [\mathbf{r}_1 - (\mathbf{r}_2 - \mathbf{R}_l)]|^{-1}$, $G_1(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s)$ can be written as [19]

$$\begin{aligned} G_1(pqrs\mathbf{k}_p\mathbf{k}_r\mathbf{k}_s) = {} & \delta_{pr}\delta_{qs}\sum_{\mathbf{R}_l\notin \mathrm{V}}\frac{1}{R_l}e^{i(\mathbf{k}_p-\mathbf{k}_r)\cdot\mathbf{R}_l} - (d_{pr}^{\mathbf{k}_r}\delta_{qs} + \delta_{pr}d_{qs}^{\mathbf{k}_s})\sum_{\mathbf{R}_l\notin \mathrm{V}}\left(\nabla\frac{1}{R_l}\right)e^{i(\mathbf{k}_p-\mathbf{k}_r)\cdot\mathbf{R}_l} \\ & + (\mathbf{D}_{pr}^{\mathbf{k}_r}\delta_{qs} - \mathbf{d}_{pr}^{\mathbf{k}_r}\mathbf{d}_{qs}^{\mathbf{k}_s} - \mathbf{d}_{qs}^{\mathbf{k}_s}\mathbf{d}_{pr}^{\mathbf{k}_r} + \delta_{pr}\mathbf{D}_{qs}^{\mathbf{k}_s})\sum_{\mathbf{R}_l\notin \mathrm{V}}\left(\nabla\nabla\frac{1}{R_l}\right)e^{i(\mathbf{k}_p-\mathbf{k}_r)\cdot\mathbf{R}_l} + \cdots, \end{aligned} \qquad (7)$$

where

$$\mathbf{d}_{pq}^{\mathbf{k}} = \sum_{\mathbf{R}_l} e^{i\mathbf{k}\cdot\mathbf{R}_l}\langle\omega_p(\mathbf{r})\,|\mathbf{r}|\omega_q(\mathbf{r}-\mathbf{R}_l)\rangle \qquad (8)$$

and

$$\mathbf{D}_{pq}^{\mathbf{k}} = \sum_{\mathbf{R}_l} e^{i\mathbf{k}\cdot\mathbf{R}_l}\langle\omega_p(\mathbf{r})\,|\mathbf{r}\mathbf{r}|\omega_q(\mathbf{r}-\mathbf{R}_l)\rangle \qquad (9)$$

converges exponentially with $\mathbf{R}_l$. Since Wannier functions are smooth, the Taylor series in Eq. (7) converges rapidly.

The second-order correction to the total energy per unit cell for closed shells is given by [15]

$$E_{\mathrm{uc}}^{(2)} = \frac{1}{W^3}\sum_{ijab}\int_{\mathrm{BZ}}d\mathbf{k}_i\int_{\mathrm{BZ}}d\mathbf{k}_a\int_{\mathrm{BZ}}d\mathbf{k}_b\,\frac{2|G(ijab\mathbf{k}_i\mathbf{k}_a\mathbf{k}_b)|^2 - \mathrm{Re}[G(ijab\mathbf{k}_i\mathbf{k}_a\mathbf{k}_b)G^*(ijba\mathbf{k}_i\mathbf{k}_b\mathbf{k}_a)]}{\epsilon_{i\mathbf{k}_i}^{\mathrm{HF}} + \epsilon_{jT(\mathbf{k}_a+\mathbf{k}_b-\mathbf{k}_i)}^{\mathrm{HF}} - \epsilon_{a\mathbf{k}_a}^{\mathrm{HF}} - \epsilon_{b\mathbf{k}_b}^{\mathrm{HF}}}\,, \qquad (10)$$

where BZ denotes the first Brillouin zone in reciprocal space, W is the volume of BZ, $\epsilon_{p\mathbf{k}}^{\mathrm{HF}}$ are HF orbital energies, and i, j and a, b denote valence and conduction bands, respectively. Since i, j can never be identical to a, b, G functions for the two-electron integrals in Eq. (10) become

$$G_1(ijab\mathbf{k}_i\mathbf{k}_a\mathbf{k}_b) = -\frac{2}{a^3}(\mathbf{d}_{ia}^{\mathbf{k}_a}\mathbf{d}_{jb}^{\mathbf{k}_b} + \mathbf{d}_{jb}^{\mathbf{k}_b}\mathbf{d}_{ia}^{\mathbf{k}_a}) \times \sum_{l>N_0}\frac{1}{l^3}\cos[(\mathbf{k}_i - \mathbf{k}_a)\cdot\mathbf{R}_l] + \cdots \qquad (11)$$

for the one-dimensional infinite chain, where a is the length of unit cell. Substituting Eqs. (5), (6), and (11) into Eq. (10) and integrating over $\mathbf{k}_i$, $\mathbf{k}_a$, $\mathbf{k}_b$, we get

$$E_{\mathrm{uc}}^{(2)} = A + 3B\sum_{l>N_0}\frac{1}{l^4} + \cdots, \qquad (12)$$

where A and B are constants and use has been made of the fact that the integration over $\mathbf{k}_i$ or $\mathbf{k}_a$ space brings a factor $1/l$ since it is a Fourier transformation [22].

In real calculations, we cannot sum over $\mathbf{R}_l$ to infinity. We have to effect a cutoff somewhere, say $l \leq N$, where $N \geq N_0$, e.g., only $2N + 1$ unit cells are included in the lattice summations. Then we can obtain an approximate value $E_{\mathrm{uc}}^{(2)}(N)$ for $E_{\mathrm{uc}}^{(2)}$. From Eq. (12), we know that

$$E_{\mathrm{uc}}^{(2)}(N) = E_{\mathrm{uc}}^{(2)} - B/N^3 + \cdots, \qquad N > N_0. \qquad (13)$$

This means that $E_{\mathrm{uc}}^{(2)}$ in polymers converges with the lattice summation at least as fast as $1/N^3$.

Figure 1 demonstrates the convergence behavior of the total energy per unit cell with a lattice summation cutoff, R_N. The calculation is for polyacetylene with unit cell C_2H_2 and basis set STO-3G. With the abscissa $1/N^3$, the values of $E_{\mathrm{uc}}^{(2)}$ for $N = 5$–7 fall perfectly on a straight line. This means that Eq. (13) describes the convergence

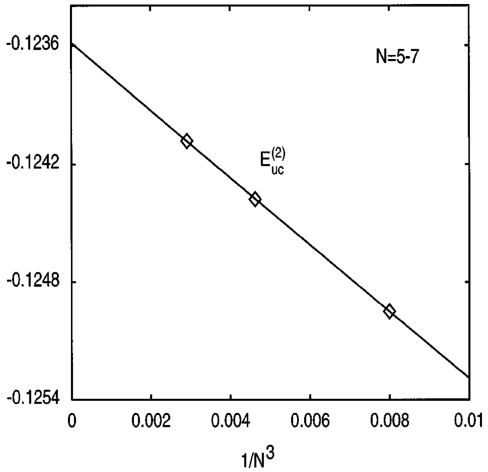

FIG. 1. Convergence behavior of total energy per unit cell with lattice summation cutoff N. The number of unit cells in the summation is $2N + 1$.

behavior very well after $N \geq 5$. We also have calculated $E_{\mathrm{uc}}^{(2)}(N)$ for $N = 2$–4. They are obviously not on the line. This situation corresponds to N being smaller than N_0. Then we can conclude that $N_0 = 5$ for polyacetylene with basis STO-3G, consistent with the sizes of Wannier functions obtained by Suhai with optimization over the phases of the Bloch orbitals [2]. One must keep in mind that the size of a Wannier orbital is just an approximate concept. It means only that the tail of the Wannier function beyond the range defined by the size is negligible for a given accuracy.

Our calculation was done with arbitary phases for Bloch orbitals. In fact, it can be seen from Eq. (10) that adding phases to Bloch orbitals does not change the numerical results at all, although it may change the size of the Wannier orbitals associated with the Bloch orbitals. This means Eq. (13) is *an intrinsic property of the system* and N_0 is determined by the size of the best localized Wannier orbitals.

The quasiparticle band energies are defined as the electron ionization potentials for valence bands and electron affinities for conduction bands with a different sign. The MBPT(2) expression for the quasiparticle band energy is

$$\epsilon_P^{\mathrm{MBPT(2)}} = \epsilon_P^{\mathrm{HF}} + \epsilon_P^{(2)}, \tag{14}$$

where P can be either an occupied or unoccupied orbital, ϵ_P^{HF} is the HF band energy, and $\epsilon_P^{(2)}$ is the MBPT(2) correction to the band energy. $\epsilon_P^{(2)}$ can be calculated by [15,16]

$$\epsilon_P^{(2)} = U_P + V_P, \tag{15}$$

where

$$U_P = \sum_I \sum_{AB} \frac{2|\langle PI \,|\, AB\rangle|^2 - \mathrm{Re}[\langle PI \,|\, AB\rangle \langle BA \,|\, PI\rangle]}{\epsilon_P^{\mathrm{HF}} + \epsilon_I^{\mathrm{HF}} - \epsilon_A^{\mathrm{HF}} - \epsilon_B^{\mathrm{HF}}}, \tag{16}$$

$$V_P = \sum_{IJ} \sum_{A} \frac{2|\langle PA \,|\, IJ\rangle|^2 - \mathrm{Re}[\langle PA \,|\, IJ\rangle \langle JI \,|\, PA\rangle]}{\epsilon_P^{\mathrm{HF}} + \epsilon_A^{\mathrm{HF}} - \epsilon_I^{\mathrm{HF}} - \epsilon_J^{\mathrm{HF}}}. \tag{17}$$

For an occupied orbital I_0, the G_1 function becomes

$$G_1(i_0 iab\mathbf{k}_{i_0}\mathbf{k}_a\mathbf{k}_b) = -(\mathbf{d}_{i_0 a}^{\mathbf{k}_a}\mathbf{d}_{jb}^{\mathbf{k}_b} + \mathbf{d}_{ib}^{\mathbf{k}_b}\mathbf{d}_{i_0 a}^{\mathbf{k}_a}) \times \sum_{\mathbf{R}_l \overline{\in} \mathrm{V}} \left(\nabla\nabla \frac{1}{R_l}\right) e^{i(\mathbf{k}_{i_0} - \mathbf{k}_a)\cdot \mathbf{R}_l} + \cdots, \tag{18}$$

for U_{i_0} and

$$G_1(i_0 aij\mathbf{k}_{i_0}\mathbf{k}_i\mathbf{k}_j) = \delta_{i_0 i} d_{aj}^{\mathbf{k}_j} \sum_{\mathbf{R}_{l'} \overline{\in} \mathrm{V}} \left(\nabla \frac{1}{R_l}\right) e^{i(\mathbf{k}_{i_0} - \mathbf{k}_i)\cdot \mathbf{R}_l} + \cdots, \tag{19}$$

for V_{i_0}. Similarly, as we did for the total energy per unit cell, we obtain

$$U_{i_0}(N) = U_{i_0} - C_{i_0}/N^3 + \cdots, \qquad N > N_0, \tag{20}$$

$$V_{i_0}(N) = V_{i_0} - D_{i_0}/N^2 + \cdots, \qquad N > N_0, \tag{21}$$

where C_{i_0} and D_{i_0} are constants. Thus we know that V_{i_0} converges one order slower than U_{i_0} and $E_{\mathrm{uc}}^{(2)}$ and so does $\epsilon_{i_0}^{(2)}$. For an unoccupied orbital a_0, the convergence properties of U_{a_0} and V_{a_0} are just the reverse of those for occupied oritials, i.e.,

$$U_{a_0}(N) = U_{a_0} - C_{a_0}/N^2 + \cdots, \qquad N > N_0, \tag{22}$$

$$V_{a_0}(N) = V_{a_0} - D_{a_0}/N^3 + \cdots, \qquad N > N_0. \tag{23}$$

Now let us take the highest occupied, $(v, \max)$, and lowest unoccupied, $(c, \min)$, orbitals in polyacetylene as examples to demonstrate the convergence behavior of U_P and V_P with N. From Eqs. (20)–(23), we know that $U_{v,\max}$ and $V_{c,\min}$ converge as $1/N^3$ with N when $N \geq N_0$ while $U_{c,\min}$ and $V_{v,\max}$ converge one power slower. Figures 2 and 3 show the numerical results

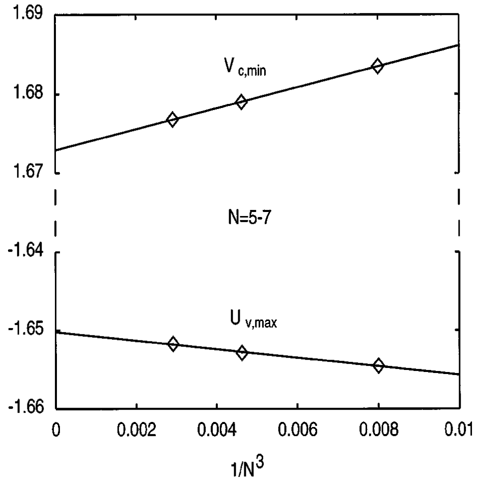

FIG. 2. Convergence behavior of $V_{c,\min}$ and $U_{v,\max}$ with N, where $(c, \min)$ and $(v, \max)$ represent the lowest unoccupied and highest occupied orbitals, respectively.

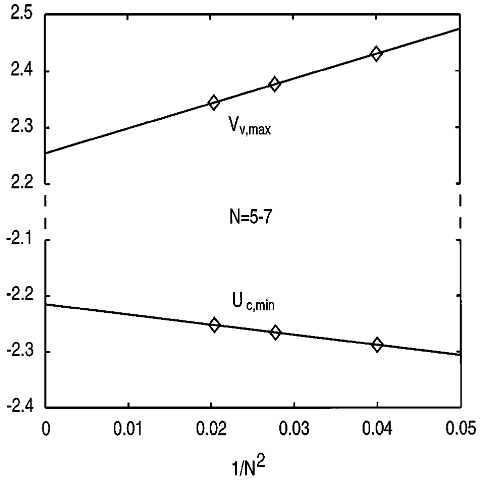

FIG. 3. Convergence behavior of $U_{c,\mathrm{min}}$ and $V_{v,\mathrm{max}}$ with N. They converge a power slower than $E_{\mathrm{uc}}^{(2)}$, $V_{c,\mathrm{min}}$, and $U_{v,\mathrm{max}}$.

calculated with a STO-3G basis, for illustration. As for $E_{\mathrm{uc}}^{(2)}$, all the numerical results for U_{i_0}, V_{i_0}, U_{a_0}, and V_{a_0} fit the corresponding formulas well for $N \geq 5$, but not for $N < 5$. This further confirms that the optimized Wannier functions span about five unit cells on each side of the reference cell.

Since the sizes of Wannier functions depend on the basis set, N_0 could be larger for a larger basis set. It is also possible for a large basis set that the coefficients for higher terms in Eqs. (13) and (20)–(23) are larger. However, we can always find a N_0 which is large enough that the higher orders can be negligible and these equations can be used to extrapolate the numerical MBPT(2) corrections obtained with a finite size of the lattice summations to infinite size. The values of the curves in Figs. 1, 2, and 3 at the origin of the abscissa are those of the quantities computed with a STO-3G basis for infinite lattice size.

In conclusion, we have obtained the explicit convergence formulas for the MBPT(2) correction to the total energy per unit cell and for the band structure in polymers. These formulas demonstrate that electron correlation has a long range effect, especially for the band energy. The formulas provide tools to guarantee fully converged MBPT(2) results via extrapolation. Similar convergence behavior can also be drawn for the corrections in two- and three-dimensional systems [23].

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