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Brueckner–Goldstone quantum Monte Carlo for correlation energies and quasiparticle energy bands of one-dimensional solids

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A new quantum Monte Carlo (QMC) method that combines the second-order many-body perturbation theory and Monte Carlo (MC) integration has been developed for correlation and correlation-corrected (quasiparticle) energy bands of one-dimensional solids. The sum-of-product expressions of correlation energy and self-energy are transformed, with the aid of a Laplace transform, into high-dimensional integrals, which are subject to a highly scalable MC integration with the Metropolis algorithm for importance sampling. The method can compute correlation energies of polyacetylene and polyethylene within a few mE_h and quasiparticle energy bands within a few tenths of an eV. It does not suffer from the fermion sign problem and its description can be systematically improved by raising the perturbation order.

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Energy bands, observable by angle-resolved photoemission spectroscopy, are central to characterizing a solid and have been the main concern of solid-state physics. Density-functional theory is well documented to be unreliable[1] and many-body methods such as the *GW* methods[2] and many-body perturbation theory (MBPT)[3] are needed for their accurate prediction. However, they inevitably involve large tensor contractions, which are fundamentally nonscalable with respect to both system size and computer size. Stochastic methods such as those in quantum Monte Carlo (QMC)[4,5] are intrinsically more scalable, but they have difficulty in calculating energy differences owing to the noise in total energies and unknown nodal structures of excited and ground states (the fermion sign problem). QMC thus cannot easily compute energy bands as continuous functions of k.

Here, capitalizing on our recent work on molecules,[6–9] we report a method that combines second-order MBPT with the Møller–Plesset partitioning of the Hamiltonian (MP2) and a stochastic algorithm for energies and quasiparticle energy bands of one-dimensional solids. It inherits the systematic, converging nature of MBPT and a scalable and easily implemented Metropolis algorithm of the Monte Carlo (MC) integration. We rewrite each of the diagrammatic expressions of these quantities from an extremely long sum-of-product of lower-dimensional integrals into a single high-dimensional integral using a Laplace transform, which is then evaluated by an MC method. Quasiparticle energies are obtained directly as stochastically integrated self-energies and not as small differences between noisy total energies. No assumed nodal structure of a wave function is needed. The resulting method, extensible to higher orders of MBPT,[9] is thus a new branch of QMC and may be called Brueckner–Goldstone QMC.

Our work is, therefore, in the same spirit as recent intense efforts by others[10–13] that "wed" *ab initio* molecular orbital theory with stochastic algorithms. However, ours stands apart in the following respects: (1) Walkers in our method roam around in real space as opposed to configuration space and there is no need for *any* molecular integrals in *any* basis, which are expensive to compute. The transformation of these integrals from the atomic-orbital (AO) to crystal-orbital (CO) basis, whose cost scales as the fifth power of system size, constitutes the computational bottleneck of MP2, which is eliminated entirely in our method; (2) It is thus fundamentally more efficient than the others and can be applied to large molecules and solids; (3) It can compute quasiparticle energy bands and correlation energies on an equal footing; (4) It shares with some of these methods the advantage that there is no fermion sign problem. However, this comes at the expense of having a bias (from the exact result) and, at higher orders, the bias will be reduced, but the sign problem will likely be reintroduced.

The second-order correction to the Hartree–Fock (HF) energy per unit cell of a one-dimensional solid[14–16] is

$$E^{(2)} = E^{(\mathrm{A})} + E^{(\mathrm{B})}, \tag{1}$$

with

$$E^{(\mathrm{A})} = \frac{2}{K}\sum_{i,j}^{\mathrm{occ.}}\sum_{a,b}^{\mathrm{vir.}}\sum_{k_i,k_j,k_a}\frac{v_{ak_ak_bk_b}^{ik_ijk_j}v_{ik_ijk_j}^{ak_ak_bk_b}}{\epsilon_{ik_i}+\epsilon_{jk_j}-\epsilon_{ak_a}-\epsilon_{bk_b}}, \tag{2}$$

$$E^{(\mathrm{B})} = \frac{-1}{K}\sum_{i,j}^{\mathrm{occ.}}\sum_{a,b}^{\mathrm{vir.}}\sum_{k_i,k_j,k_a}\frac{v_{ak_ak_bk_b}^{ik_ijk_j}v_{jk_jik_i}^{ak_ak_bk_b}}{\epsilon_{ik_i}+\epsilon_{jk_j}-\epsilon_{ak_a}-\epsilon_{bk_b}}, \tag{3}$$

where ϵ_{pk_p} is the HF orbital energy of the state in the pth band and wave vector k_p and K is the number of evenly spaced wave vector sampling points in the Brillouin zone (BZ). Each wave vector is confined within the first BZ, $0 \le k_p < 2\pi/l$, where l is the lattice constant, and only three of the four wave vectors are linearly independent because $k_b = k_i + k_j - k_a + 2n\pi/l$ (n is an integer) owing to the momentum conservation law.

The two-electron integral is given by

$$v_{ak_ak_bk_b}^{ik_ijk_j} = K\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\varphi_{ik_i}^{(0)*}(\mathbf{r}_1)\varphi_{jk_j}^{(L)*}(\mathbf{r}_2)\varphi_{ak_a}^{(S)}(\mathbf{r}_1)\varphi_{bk_b}^{(L+S)}(\mathbf{r}_2)}{r_{12}} \tag{4}$$

with

$$\varphi_{pk_p}^{(M)}(\mathbf{r}) = K^{-1/2}\sum_{m=-M}^{+M} C_{pk_p}^{\mu} e^{imk_pa}\chi_{\mu(m)}(\mathbf{r}), \tag{5}$$

where $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$, $\varphi_{pk_p}(\mathbf{r})$ is the CO spanning $2M + 1$ unit cells, $\chi_{\mu(m)}(\mathbf{r})$ is the μth AO in the mth unit cell, and $C^{\mu}_{pk_p}$ is the CO expansion coefficient. The summations over the unit-cell indices are truncated at the short- (S) and long-range (L) cutoffs in accordance with the logic analogous to the one underlying the Namur cutoff criterion.[17] The two-electron integral displays the $O(K^{-1})$ dependence.

In the diagonal and adiabatic approximations to the self-energy, the second-order correlation-corrected orbital energy[14–16] is given by

$$\epsilon^{(2)}_{pk_p} = \epsilon_{pk_p} + \Sigma^{(\mathrm{C})}_{pk_p} + \Sigma^{(\mathrm{D})}_{pk_p} + \Sigma^{(\mathrm{E})}_{pk_p} + \Sigma^{(\mathrm{F})}_{pk_p}, \tag{6}$$

with

$$\Sigma^{(\mathrm{C})}_{pk_p} = 2 \sum_{j}^{\text{occ.}} \sum_{a,b}^{\text{vir.}} \sum_{k_j,k_a} \frac{v^{pk_p jk_j}_{ak_a bk_b} v^{ak_a bk_b}_{pk_p jk_j}}{\epsilon_{pk_p} + \epsilon_{jk_j} - \epsilon_{ak_a} - \epsilon_{bk_b}}, \tag{7}$$

$$\Sigma^{(\mathrm{D})}_{pk_p} = -\sum_{j}^{\text{occ.}} \sum_{a,b}^{\text{vir.}} \sum_{k_j,k_a} \frac{v^{pk_p jk_j}_{ak_a bk_b} v^{ak_a bk_b}_{jk_j pk_p}}{\epsilon_{pk_p} + \epsilon_{jk_j} - \epsilon_{ak_a} - \epsilon_{bk_b}}, \tag{8}$$

$$\Sigma^{(\mathrm{E})}_{pk_p} = -2 \sum_{i,j}^{\text{occ.}} \sum_{b}^{\text{vir.}} \sum_{k_i,k_j} \frac{v^{ik_i jk_j}_{pk_p bk_b} v^{pk_p bk_b}_{ik_i jk_j}}{\epsilon_{ik_i} + \epsilon_{jk_j} - \epsilon_{pk_p} - \epsilon_{bk_b}}, \tag{9}$$

$$\Sigma^{(\mathrm{F})}_{pk_p} = \sum_{i,j}^{\text{occ.}} \sum_{b}^{\text{vir.}} \sum_{k_i,k_j} \frac{v^{ik_i jk_j}_{pk_p bk_b} v^{pk_p bk_b}_{jk_j ik_i}}{\epsilon_{ik_i} + \epsilon_{jk_j} - \epsilon_{pk_p} - \epsilon_{bk_b}}. \tag{10}$$

A plot of $\epsilon^{(2)}_{pk_p}$ as a function of k_p is the quasiparticle energy bands. They are reliable when

$$\epsilon_{\mathrm{HOCO}} - E_{\mathrm{g}} < \epsilon_{pk_p} < \epsilon_{\mathrm{LUCO}} + E_{\mathrm{g}}, \tag{11}$$

where $E_{\mathrm{g}} = \epsilon_{\mathrm{LUCO}} - \epsilon_{\mathrm{HOCO}}$ and HOCO and LUCO stand for the highest occupied CO (valence band edge) and lowest unoccupied CO (conduction band edge) of the HF theory, respectively. However, they tend to display signs of divergence outside this domain as the denominators in Eqs. (7)–(10) can become zero.

Here, we propose a transformation of each of the above sum-of-product matrix equations of MP2 into the form that lends itself to a more scalable MC integration, that is, a single high-dimensional integral. Using the Laplace transform,[18]

$$\frac{1}{\epsilon_{ik_i} + \epsilon_{jk_j} - \epsilon_{ak_a} - \epsilon_{bk_b}} = -\int_0^\infty d\tau\, e^{(\epsilon_{ik_i} + \epsilon_{jk_j} - \epsilon_{ak_a} - \epsilon_{bk_b})\tau}, \tag{12}$$

one can interchange the order of summations and integrations to rewrite Eq. (2) into a 16-dimensional integral,

$$E^{(\mathrm{A})} = \frac{l^3}{(2\pi)^3} \iiiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \iiint dk_i dk_j dk_a \int_0^\infty d\tau \times f_{\mathrm{A}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, k_i, k_j, k_a, \tau) \tag{13}$$

$$\approx \frac{1}{N} \sum_{n=1}^{N} \frac{\tilde{f}_{\mathrm{A}}(\mathbf{r}^{[n]}_1, \mathbf{r}^{[n]}_2, \mathbf{r}^{[n]}_3, \mathbf{r}^{[n]}_4)}{w(\mathbf{r}^{[n]}_1, \mathbf{r}^{[n]}_2, \mathbf{r}^{[n]}_3, \mathbf{r}^{[n]}_4)} \equiv \frac{1}{N} \sum_{n=1}^{N} I^{(\mathrm{A})}_n \equiv I^{(\mathrm{A})}_N, \tag{14}$$

with

$$f_{\mathrm{A}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, k_i, k_j, k_a, \tau) = \frac{-2K}{r_{12} r_{34}} G^{(0)}_-(\mathbf{r}_1, \mathbf{r}_3, k_i, \tau) G^{(L)}_-(\mathbf{r}_2, \mathbf{r}_4, k_j, \tau) \times G^{(S)}_+(\mathbf{r}_1, \mathbf{r}_3, k_a, \tau) G^{(L+S)}_+(\mathbf{r}_2, \mathbf{r}_4, k_b, \tau), \tag{15}$$

where $G^{(M)}_+$ and $G^{(M)}_-$ are the traces of the retarded and advanced Green's functions, respectively, and defined[9] as

$$G^{(M)}_-(\mathbf{r}_1, \mathbf{r}_3, k_i, \tau) = \sum_{i}^{\text{occ.}} \varphi^{(M)*}_{ik_i}(\mathbf{r}_1) \varphi^{(M)}_{ik_i}(\mathbf{r}_3) e^{\epsilon_{ik_i}\tau}, \tag{16}$$

$$G^{(M)}_+(\mathbf{r}_1, \mathbf{r}_3, k_a, \tau) = \sum_{a}^{\text{vir.}} \varphi^{(M)}_{ak_a}(\mathbf{r}_1) \varphi^{(M)*}_{ak_a}(\mathbf{r}_3) e^{-\epsilon_{ak_a}\tau}. \tag{17}$$

Equation (3) for $E^{(\mathrm{B})}$ can be likewise written as a single integral.

Equation (14) illustrates how the 16-dimensional integral of Eq. (13) can be evaluated by an MC method as a sum of the ratios of the modified integrand $\tilde{f}_{\mathrm{A}}$ to the weight function w at sampling points $\{\mathbf{r}^{[n]}_1, \mathbf{r}^{[n]}_2, \mathbf{r}^{[n]}_3, \mathbf{r}^{[n]}_4\}$ distributed randomly but according to the weight function w. Here, N is the number of MC sampling points or steps and $\tilde{f}_{\mathrm{A}}$ is the integral of f_{A} over k_i, k_j, and k_a using a mixed quadrature-MC method (see below) and over τ evaluated by the 21-point Gauss–Kronrod quadrature,[19]

$$\tilde{f}_{\mathrm{A}} = \frac{l^3}{(2\pi)^3} \iiint dk_i dk_j dk_a \int_0^\infty d\tau\, f_{\mathrm{A}}(\ldots, k_i, k_j, k_a, \tau) \approx \sum_{i=1}^{K} \sum_{j=1}^{K} \sum_{a=1}^{K} \sum_{m=1}^{21} w_m f_{\mathrm{A}}\left(\ldots, \frac{2\pi}{l}\frac{i}{K}, \frac{2\pi}{l}\frac{j}{K}, \frac{2\pi}{l}\frac{a}{K}, \tau_m\right), \tag{18}$$

where τ_m and w_m are the coordinate and weight of the mth Gauss–Kronrod grid point and k_b is determined by the momentum conservation law. It is readily verified that $E^{(\mathrm{A})}$ (energy per unit cell) scales as $O(K^0)$ and is thermodynamically intensive.

The weight function is the product,

$$w(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = w(\mathbf{r}_1, \mathbf{r}_2) w(\mathbf{r}_3, \mathbf{r}_4), \tag{19}$$

with

$$w(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{J} \sum_{m=-L}^{+L} \frac{\rho_{(0)}(\mathbf{r}_1) \rho_{(m)}(\mathbf{r}_2)}{r_{12}}, \tag{20}$$

and

$$J = \sum_{m=-L}^{+L} \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_{(0)}(\mathbf{r}_1) \rho_{(m)}(\mathbf{r}_2)}{r_{12}}, \tag{21}$$

where $\rho_{(m)}$ is the electron density of the mth unit cell or, more preferably, the sum of diffuse s-type Gaussian-type orbitals centered in the mth unit cell; the diffuseness causes oversampling, which is less harmful than undersampling. In either case, the weight function is nonnegative and J can be evaluated analytically.[20]

One of the self-energy diagrams [Eq. (7)] can be expressed as a single 15-dimensional integral,

$$\Sigma^{(\mathrm{C})}_{pk_p} = \frac{l^2}{(2\pi)^2} \iiiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \iint dk_j dk_a \int_0^\infty d\tau \times f_{\mathrm{C}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, k_j, k_a, \tau) \quad (22)$$

$$\approx \frac{1}{N} \sum_{n=1}^{N} \frac{\tilde{f}_{\mathrm{C}}(\mathbf{r}_1^{[n]}, \mathbf{r}_2^{[n]}, \mathbf{r}_3^{[n]}, \mathbf{r}_4^{[n]})}{w(\mathbf{r}_1^{[n]}, \mathbf{r}_2^{[n]}, \mathbf{r}_3^{[n]}, \mathbf{r}_4^{[n]})}, \quad (23)$$

where

$$f_{\mathrm{C}}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, k_j, k_a, \tau) = \frac{-2K^2}{r_{12} r_{34}} \varphi^{(0)*}_{pk_p}(\mathbf{r}_1) \varphi^{(0)}_{pk_p}(\mathbf{r}_3) e^{\epsilon_{ik_i}\tau} \times G^{(L)}_{-}(\mathbf{r}_2, \mathbf{r}_4, k_j, \tau) G^{(S)}_{+}(\mathbf{r}_1, \mathbf{r}_3, k_a, \tau) G^{(L+S)}_{+}(\mathbf{r}_2, \mathbf{r}_4, k_b, \tau) \quad (24)$$

using the Laplace transform,

$$\frac{1}{\epsilon_{pk_p} + \epsilon_{jk_j} - \epsilon_{ak_a} - \epsilon_{bk_b}} = -\int_0^\infty d\tau\, e^{(\epsilon_{pk_p} + \epsilon_{jk_j} - \epsilon_{ak_a} - \epsilon_{bk_b})\tau}. \quad (25)$$

Note that this transformation is valid if and only if the denominator in the left-hand side is negative and this is guaranteed by the condition of Eq. (11).

The other three terms in Eq. (6) are likewise converted into single integrals, which are subject to an MC integration. As suggested by Eq. (23), the above integral can be evaluated using the same weight function as Eq. (19). Hence, $\tilde{f}_{\mathrm{C}}$ is given by

$$\tilde{f}_{\mathrm{C}} = \frac{l^2}{(2\pi)^2} \iint dk_j dk_a \int_0^\infty d\tau\, f_{\mathrm{A}}(\ldots, k_j, k_a, \tau) \approx \sum_{j=1}^{K} \sum_{a=1}^{K} \sum_{m=1}^{21} w_m f_{\mathrm{C}}\left(\ldots, \frac{2\pi}{l}\frac{j}{K}, \frac{2\pi}{l}\frac{a}{K}, \tau_m\right). \quad (26)$$

Self-energy $\Sigma^{(\mathrm{C})}_{pk_p}$ scales as $O(K^0)$ as it should.

The algorithm consists of three steps: (1) Electron walker pairs are propagated using the Metropolis algorithm according to the weight function $w(\mathbf{r}_1, \mathbf{r}_2)$ defined by Eq. (20). The number of pairs is two at minimum ($\{\mathbf{r}_1, \mathbf{r}_2\}$ and $\{\mathbf{r}_3, \mathbf{r}_4\}$), but much more than two (say, m) are used in practice to adopt the redundant-walker algorithm,[8] which increases the sampling efficiency by $O(m)$. (2) When the Metropolis move is accepted, CO's and other factors in the integrands are evaluated at the walker pair coordinates, a set of k's and τ's. In this particular implementation, the values of k_j and k_a are randomly distributed on an evenly spaced grid with K points, while k_i and k_p go over all K points. The integration over k_i, therefore, uses the trapezoidal rule and those over k_j and k_a an MC method with the number of (k_j, k_a) per step being just one. In this way, the correlation and self-energy calculations can share intermediate data. (3) The integrands are evaluated and accumulated into $I^{(A)}_N$, etc. The statistical uncertainty (σ) in the MC-evaluated $E^{(\mathrm{A})}$ is then estimated by

$$\sigma^2 = \frac{1}{N(N-1)} \sum_{n=1}^{N} \left\{ I^{(\mathrm{A})}_n - I^{(\mathrm{A})}_N \right\} \quad (27)$$

TABLE I. The second-order correlation corrections ($E^{(2)}$) per C_2H_2 or C_2H_4 unit cell to the HF energies of polyacetylene and polyethylene and associated statistical uncertainties (σ) in E_{h}. The number of MC steps (N) is 5×10^6, the number of redundant walker pairs (m) is 15, the number of k points (K) is 20, $S = 4$, and $L = 2$. The geometries are taken from Ref. 22.

System	Method	$E^{(2)}$	σ
Polyacetylene	MP2/6-31G	−0.1728	···
Polyacetylene	MC-MP2/6-31G	−0.1783	0.0036
Polyethylene	MP2/6-31G	−0.1827	···
Polyethylene	MC-MP2/6-31G	−0.1807	0.0065

and similarly for other quantities; this formula, however, underestimates σ.[21] Clearly, the whole process can be easily and efficiently parallelized.[8]

Figure 1 shows the convergence of the MP2 correlation energy of an infinitely extended chain of polyacetylene under the periodic boundary condition using the MC method (MC-MP2). Two s-type Gaussian-type orbitals per atom are used as the weight function with $S = 4$, $L = 2$, 15 redundant walker pairs, and 20 k points. A smooth convergence to the correct deterministic value of the correlation energy is observed, with the expected $N^{-1/2}$ falloff of the statistical uncertainty (σ). The numerical values at $N = 5 \times 10^6$ are compiled in Table I for polyacetylene and also for polyethylene. The data confirm that MC-MP2 reproduce the correct results for two systems within a few mE_{h} and 3σ.

Figure 2 compares the correlation-corrected (i.e., quasiparticle) energy bands calculated from MP2 and MC-MP2 for polyacetylene and polyethylene. HF energy bands are also superimposed merely to emphasize the importance of electron correlation; band gaps and widths are exaggerated in HF, as is well known. For polyacetylene (the left panel), the MC-MP2 results for HOCO and LUCO are rapidly convergent and fall nearly exactly on the MP2 energy bands. The statistical uncertainties are a few tenths of an eV. For polyethylene (the right panel), HOCO, LUCO, and two higher and lower lying bands are computed by MC-MP2 to demonstrate that the method works not just for the valence and conduction bands, which are treatable by electron addition or subtraction in QMC,[23] but also for higher- or lower-lying bands. In this case, the occupied bands obtained by MC-MP2 are rapidly converged and in accurate agreement with the deterministic results as well as with the experimental data (but not with the HF results). On the other hand, the conduction band obtained by MC-MP2 near $k = \pi/l$ suffers from larger statistical uncertainties, while there seem no evidence of a bias (from the deterministic MP2 results).

Diffusion Monte Carlo (DMC) has been applied to excited states with assumed nodal structures to compute band gaps[24] and energy bands at some points in BZ.[25] A new QMC method for excited states, dubbed correlation function QMC,[26] has been developed. Auxiliary-field QMC (AFQMC), using an excited-state determinant as an auxiliary field, has also been successful in obtaining band gaps.[27] They have difficulty obtaining bands as continuous functions of k. As compared with

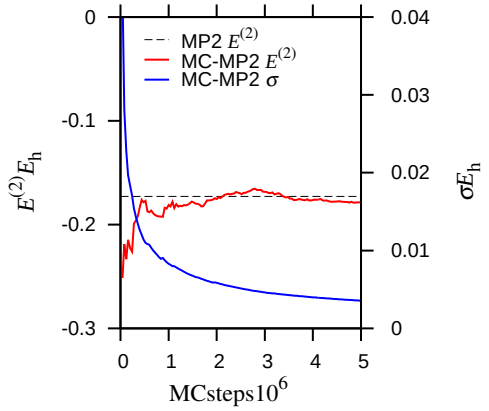

FIG. 1. Convergence of MC-MP2 correlation energy of polyacetylene.

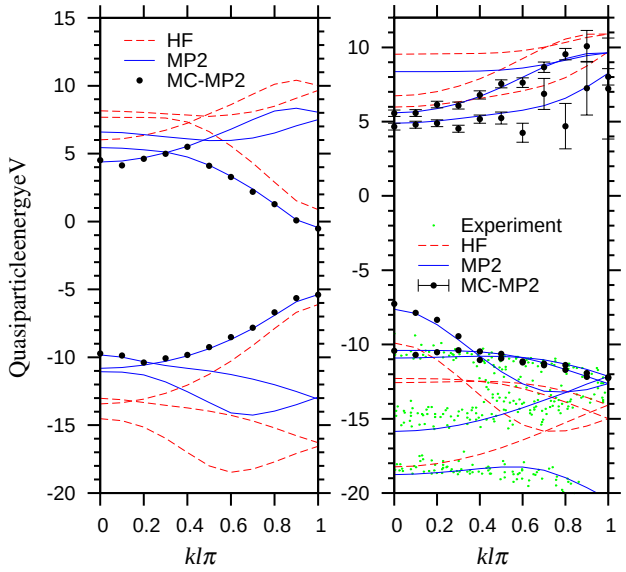

FIG. 2. (Left) HF energy band and MP2 and MC-MP2 quasiparticle energy bands of polyacetylene. The statistical uncertainties are smaller than the diameter of the filled circles. (Right) The same as the left panel but for polyethylene. Larger statistical uncertainties are shown as error bars. The experimental results are due to Ueno *et al.*[29].

these, MC-MP2 is capable of computing parameters at any k point and any energy band [within the constraint of Eq. (11)] without a case-by-case definition of excited-state wave function structures. Conversely, MC-MP2 is farther from exactness than DMC or AFQMC, though MC-MP2 has the advantage of being systematic.[9] The fourth-order MP method is known to be generally as accurate as the coupled-cluster singles, doubles, and non-iterative triples [CCSD(T)] method[28], which is widely used for molecular property predictions. The MP method at any order is inapplicable to metals, however.

In summary, this article has reported a new QMC method that combines MBPT and an MC integration and can compute MP2 correlation energy and quasiparticle energy bands of a one-dimensional solid. Unlike the deterministic MBPT or MP2, its algorithm does not involve numerous tensors (molecular integrals) or their contractions, which are fundamentally nonscalable with respect to both computer and system sizes. Unlike QMC, MC-MP2 can calculate energy differences (correlation energies and energy bands) directly and is systematically improvable toward exactness in principle. MC-MP2 does not suffer from the fermion sign problem, but as a tradeoff with introducing an inevitable bias.

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