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Fast coupled-cluster singles and doubles for extended systems: Application to the anharmonic vibrational frequencies of polyethylene in the Γ approximation

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The mod-n scheme is introduced to the coupled-cluster singles and doubles (CCSD) and third-order Møller-Plesset perturbation (MP3) methods for extended systems of one-dimensional periodicity. By downsampling uniformly the wave vectors in Brillouin-zone integrations, this scheme accelerates these accurate but expensive correlation-energy calculations by two to three orders of magnitude while incurring negligible errors in their total and relative energies. To maintain this accuracy, the number of the nearest-neighbor unit cells included in the lattice sums must also be reduced by the same downsampling rate (n). The mod-n CCSD and MP3 methods are applied to the potential-energy surface of polyethylene in anharmonic frequency calculations of its infrared- and Raman-active vibrations. The calculated frequencies are found to be within 46 cm^{-1} (CCSD) and 78 cm^{-1} (MP3) of the observed.

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I. INTRODUCTION

The coupled-cluster singles and doubles (CCSD) (Refs. 1 and 2) and second-, third-, and fourth-order Møller-Plesset perturbation (MP2, MP3, and MP4) methods[1–7] have been implemented for extended systems of one-dimensional periodicity. Their formalisms and systematic accuracy for insulators and semiconductors are well documented. Their applications to crystalline polymers have, however, not been widespread owing to their immense computational cost. MP2 involves a computational step whose operational complexity increases as $O(K^3)$, where K is the number of wave vector (k vector) sampling points in the first Brillouin zone (BZ). The value of K that ensures the convergence of preceding Hartree-Fock (HF) calculations is in the range of 10–20. This implies that an MP2 calculation of a one-dimensional extended system is three to four orders of magnitude as expensive as that of a molecule of size similar to the unit cell. The K dependence of the costs of MP3 and CCSD is even worse: $O(K^4)$.

In this work, we introduce a scheme—the mod-n scheme—that reduces the effective value of K and thereby accelerates the MP3 and CCSD calculations for one-dimensional extended systems by two to three orders of magnitude with an error of a few percent in correlation energies. It is based on uniform downsampling of k vectors in BZ integrations,[8,9] which has been shown to speed up MP2 calculations by one order of magnitude (see also related exponential downsampling[10]). It proves to be even more effective for MP3 and CCSD, although the latter require an additional adjustment to their formalisms. We demonstrate the utility of mod-n MP3 and CCSD by applying them to the potential-energy surface (PES) of polyethylene in the anharmonic frequency calculations of its infrared- and Raman-active vibrations. Systematic improvements in the calculated frequencies as we increase the level of theory from MP2 to MP3 and from MP3 to CCSD implies the reliability of the relative energies obtained with this scheme.

II. COMPUTATIONAL METHOD

The MP3 and CCSD correlation energies per unit cell[2] can be obtained by evaluating

$$\begin{aligned}
E_{\mathrm{MP3}} = {}& \frac{1}{K}\sum_{i,j,a,b,c,d}\ \sum_{k_i,k_j,k_a,k_c} \frac{v^{ik_ijk_j}_{ak_abk_b} v^{ak_abk_b}_{ck_cdk_d} w^{ik_ijk_j*}_{ck_cdk_d}}{D^{ik_ijk_j}_{ak_abk_b} D^{ik_ijk_j}_{ck_cdk_d}} \\
&+ \frac{1}{K}\sum_{i,j,k,l,a,b}\ \sum_{k_i,k_j,k_k,k_a} \frac{v^{ik_ijk_j}_{ak_abk_b} v^{kk_klk_l}_{ik_ijk_j} w^{kk_klk_l*}_{ak_abk_b}}{D^{ik_ijk_j}_{ak_abk_b} D^{kk_klk_l}_{ak_abk_b}} \\
&+ \frac{4}{K}\sum_{i,j,k,a,b,c}\ \sum_{k_i,k_j,k_a,k_c} \frac{v^{ik_ijk_j}_{ak_abk_b} v^{kk_kbk_b}_{ck_cjk_j} w^{ik_ikk_k*}_{ak_ack_c}}{D^{ik_ijk_j}_{ak_abk_b} D^{ik_ikk_k}_{ak_ack_c}} \\
&- \frac{2}{K}\sum_{i,j,k,a,b,c}\ \sum_{k_i,k_j,k_a,k_c} \frac{v^{ik_ijk_j}_{ak_abk_b} v^{kk_kak_a}_{ik_ick_c} w^{jk_jkk_k*}_{bk_bck_c}}{D^{ik_ijk_j}_{ak_abk_b} D^{jk_jkk_k}_{bk_bck_c}} \\
&- \frac{2}{K}\sum_{i,j,k,a,b,c}\ \sum_{k_i,k_j,k_a,k_c} \frac{v^{ik_ijk_j}_{ak_abk_b} w^{kk_kak_a}_{jk_jck_c} v^{ik_ikk_k*}_{ck_cbk_b}}{D^{ik_ijk_j}_{ak_abk_b} D^{ik_ikk_k}_{bk_bck_c}} \\
&- \frac{2}{K}\sum_{i,j,k,a,b,c}\ \sum_{k_i,k_j,k_a,k_c} \frac{v^{ik_ijk_j}_{ak_abk_b} w^{kk_kbk_b}_{ck_cik_i} v^{jk_jkk_k*}_{ak_ack_c}}{D^{ik_ijk_j}_{ak_abk_b} D^{jk_jkk_k}_{ak_ack_c}}
\end{aligned} \tag{1}$$

and

$$\begin{aligned}
E_{\mathrm{CCSD}} = {}& \frac{2}{K}\sum_{i,a}\sum_{k_i} f^{ik_i}_{ak_a} t^{ak_a}_{ik_i} + \frac{1}{K}\sum_{i,j,a,b}\sum_{k_i,k_j} w^{ik_ijk_j}_{ak_abk_b} t^{ak_a}_{ik_i} t^{bk_b}_{jk_j} \\
&+ \frac{1}{K}\sum_{i,j,a,b}\ \sum_{k_i,k_j,k_a} w^{ik_ijk_j}_{ak_abk_b} t^{ak_abk_b}_{ik_ijk_j},
\end{aligned} \tag{2}$$

respectively, where i, j, k, and l refer to occupied bands, a, b, c, and d unoccupied bands, and D is an orbital-energy difference,

$$D^{ik_ijk_j}_{ak_abk_b} = f^{ik_i}_{ik_i} + f^{jk_j}_{jk_j} - f^{ak_a}_{ak_a} - f^{bk_b}_{bk_b}. \tag{3}$$

Each of the k vectors can take one of the K allowed values in the first BZ,

$$k=\frac{2m}{K}, \tag{4}$$

where the lattice constant a (not shown) is equal to π in our length unit and m is an integer in the range: $0\le m<K$. The evaluation of Eqs. (1) and (2) involves, respectively, $O(K^4)$ and $O(K^3)$ arithmetic operations.

The Fock (f) and two-electron integrals (v and w) in the crystal-orbital (CO) basis are defined with the corresponding quantities in the atomic-orbital (AO) basis[2] as

$$f^{ik_i}_{ak_a}=\sum_{\mu,\nu}\sum_{m=-S}^{+S}c^{\mu k_i *}_{ik_i}c^{\nu k_a}_{ak_a}\exp(ik_ima)f^{\mu(0)}_{\nu(m)}, \tag{5}$$

$$v^{ik_ijk_j}_{ak_abk_b}=\frac{1}{K}\sum_{\kappa,\lambda,\mu,\nu}\sum_{m_1=-S}^{+S}\sum_{m_2=-L}^{+L}\sum_{m_3=m_2-S}^{m_2+S}c^{\kappa k_i *}_{ik_i}c^{\lambda k_a}_{ak_a}c^{\mu k_j *}_{jk_j}c^{\nu k_b}_{bk_b}\exp\{i(m_1k_a-m_2k_j+m_3k_b)a\}v^{\kappa(0)\mu(m_2)}_{\lambda(m_1)\nu(m_3)}, \tag{6}$$

and $w^{ik_ijk_j}_{ak_abk_b}=2v^{ik_ijk_j}_{ak_abk_b}-v^{ik_ijk_j}_{bk_bak_a}$, where $c^{\mu k_i *}_{ik_i}$, $c^{\nu k_a}_{ak_a}$, etc. are CO coefficients to be determined by the HF procedure and S and L are integer parameters used in the Namur criteria for lattice summation truncations.[11] The appropriate value of L is approximately $K/2$. These integrals vanish identically unless the momentum conservation conditions are satisfied,

$$k_a-k_i=2m_1, \tag{7}$$

$$k_a+k_b-k_i-k_j=2m_2, \tag{8}$$

for one- and two-electron integrals, respectively, where m_1 and m_2 are integers. Because of these conditions, each term in Eq. (1) has only fourfold k summation though there are six distinct k vectors in the summand.

The unknown coefficients (the t amplitudes) in Eq. (2) are obtained by solving coupled nonlinear equations. These equations (the t_1- and t_2-amplitude equations) are written as

$$\begin{aligned}0={}&f^{ak_a}_{ik_i}-2\sum_{k,c}f^{kk_k}_{ck_c}t^{ak_a}_{kk_k}t^{ck_c}_{ik_i}+\sum_{c}\kappa^{ak_a}_{ck_c}t^{ck_c}_{ik_i}-\sum_{k}\kappa^{kk_k}_{ik_i}t^{ak_a}_{kk_k}\\&+\sum_{k,c}\sum_{k_k}\kappa^{kk_k}_{ck_c}(2t^{ck_cak_a}_{kk_kik_i}-t^{ck_cak_a}_{ik_ikk_k})+\sum_{k,c}\kappa^{kk_k}_{ck_c}t^{ak_a}_{kk_k}t^{ck_c}_{ik_i}\\&+\sum_{k,c}\sum_{k_k}w^{ak_akk_k}_{ik_ick_c}t^{ck_c}_{kk_k}+\sum_{k,c,d}\sum_{k_k,k_c}w^{ak_akk_k}_{ck_cdk_d}t^{ck_cdk_d}_{ik_ikk_k}\\&+\sum_{k,c,d}\sum_{k_k}w^{ak_akk_k}_{ck_cdk_d}t^{ck_c}_{ik_i}t^{dk_d}_{kk_k}-\sum_{k,l,c}\sum_{k_k,k_l}w^{kk_klk_l}_{ik_ick_c}t^{ak_ack_c}_{kk_klk_l}\\&-\sum_{k,l,c}\sum_{k_l}w^{kk_klk_l}_{ik_ick_c}t^{ak_a}_{kk_k}t^{ck_c}_{lk_l}\end{aligned} \tag{9}$$

and

$$\begin{aligned}0={}&v^{ik_ijk_j *}_{ak_abk_b}+\sum_{k,l}\sum_{k_k}\chi^{kk_klk_l}_{ik_ijk_j}t^{ak_abk_b}_{kk_klk_l}+\sum_{k,l}\chi^{kk_klk_l}_{ik_ijk_j}t^{ak_a}_{kk_k}t^{bk_b}_{lk_l}\\&+\sum_{c,d}\sum_{k_c}\chi^{ak_abk_b}_{ck_cdk_d}t^{ck_cdk_d}_{ik_ijk_j}+\sum_{c,d}\chi^{ak_abk_b}_{ck_cdk_d}t^{ck_c}_{ik_i}t^{dk_d}_{jk_j}+P\sum_{c}\lambda^{ak_a}_{ck_c}t^{ck_cbk_b}_{ik_ijk_j}\\&-P\sum_{k}\lambda^{kk_k}_{ik_i}t^{ak_abk_b}_{kk_kjk_j}+P\sum_{c}(v^{ak_abk_b}_{ik_ick_c}-\sum_{k}v^{kk_kbk_b}_{ik_ick_c}t^{ak_a}_{kk_k})t^{ck_c}_{jk_j}\\&-P\sum_{k}(v^{ak_akk_k}_{ik_ijk_j}+\sum_{c}v^{ak_akk_k}_{ik_ick_c}t^{ck_c}_{jk_j})t^{bk_b}_{kk_k}+P\sum_{k,c}\sum_{k_k}(2\chi^{ak_akk_k}_{ik_ick_c}\\&-\chi^{ak_akk_k}_{ck_cik_i})t^{ck_cbk_b}_{kk_kjk_j}-P\sum_{k,c}\sum_{k_k}\chi^{ak_akk_k}_{ik_ick_c}t^{bk_bck_c}_{kk_kjk_j}\\&-P\sum_{k,c}\sum_{k_k}\chi^{bk_bkk_k}_{ck_cik_i}t^{ak_ack_c}_{kk_kjk_j},\end{aligned} \tag{10}$$

where $P\zeta^{ak_abk_b}_{ik_ijk_j}=\zeta^{ak_abk_b}_{ik_ijk_j}+\zeta^{bk_bak_a}_{ik_ijk_j}$ with ζ designating an arbitrary tensor. The intermediate quantities (κ, λ, and χ) are defined elsewhere.[2] The cost of solving these equations scales as $O(K^4)$ because, for instance, evaluating the second term in the right-hand side of Eq. (10) involves $O(K^4)$ arithmetic operations.

Our mod-n scheme[8,9] accelerates these electron-correlation calculations by sampling only every nth of the k vectors used in the HF step. In other words, each k vector in the MP3 or CCSD step can now take one of the following K/n allowed values:

$$k=\frac{2nm}{K}, \tag{11}$$

where m is an integer in the range: $0\le nm<K$. It is stipulated that n evenly divides K. Designating this set of k vectors by $\mathbb{K}_n$, the mod-n MP3 and CCSD correlation energies are evaluated as

$$\begin{aligned}E^{(n)}_{\mathrm{MP3}}={}&\frac{n^4}{K}\sum_{i,j,a,b,c,d}\sum_{k_i,k_j,k_a,k_c\in\mathbb{K}_n}\frac{\tilde{v}^{ik_ijk_j}_{ak_abk_b}\tilde{v}^{ak_abk_b}_{ck_cdk_d}\tilde{w}^{ik_ijk_j *}_{ck_cdk_d}}{D^{ik_ijk_j}_{ak_abk_b}D^{ik_ijk_j}_{ck_cdk_d}}\\&+\frac{n^4}{K}\sum_{i,j,k,l,a,b}\sum_{k_i,k_j,k_k,k_a\in\mathbb{K}_n}\frac{\tilde{v}^{ik_ijk_j}_{ak_abk_b}\tilde{v}^{kk_klk_l}_{ik_ijk_j}\tilde{w}^{kk_klk_l *}_{ak_abk_b}}{D^{ik_ijk_j}_{ak_abk_b}D^{kk_klk_l}_{ak_abk_b}}\\&+\frac{4n^4}{K}\sum_{i,j,k,a,b,c}\sum_{k_i,k_j,k_a,k_c\in\mathbb{K}_n}\frac{\tilde{v}^{ik_ijk_j}_{ak_abk_b}\tilde{v}^{kk_kbk_b}_{ck_cjk_j}\tilde{w}^{ik_ikk_k *}_{ak_ack_c}}{D^{ik_ijk_j}_{ak_abk_b}D^{ik_ikk_k}_{ak_ack_c}}\\&-\frac{2n^4}{K}\sum_{i,j,k,a,b,c}\sum_{k_i,k_j,k_a,k_c\in\mathbb{K}_n}\frac{\tilde{v}^{ik_ijk_j}_{ak_abk_b}\tilde{v}^{kk_kak_a}_{ik_ick_c}\tilde{w}^{jk_jkk_k *}_{bk_bck_c}}{D^{ik_ijk_j}_{ak_abk_b}D^{jk_jkk_k}_{bk_bck_c}}\\&-\frac{2n^4}{K}\sum_{i,j,k,a,b,c}\sum_{k_i,k_j,k_a,k_c\in\mathbb{K}_n}\frac{\tilde{v}^{ik_ijk_j}_{ak_abk_b}\tilde{w}^{kk_kak_a}_{jk_jck_c}\tilde{v}^{ik_ikk_k *}_{ck_cbk_b}}{D^{ik_ijk_j}_{ak_abk_b}D^{ik_ikk_k}_{bk_bck_c}}\end{aligned}$$

$$-\frac{2n^4}{K}\sum_{i,j,k,a,b,c}\;\sum_{k_i,k_j,k_a,k_c\in\mathbb{K}_n}\frac{\tilde{v}^{ik_ijk_j}_{ak_abk_b}\tilde{w}^{kk_kbk_b}_{ck_cik_i}\tilde{v}^{jk_jkk_k*}_{ak_ack_c}}{D^{ik_ijk_j}_{ak_abk_b}D^{jk_jkk_k}_{ak_ack_c}} \tag{12}$$

and

$$E^{(n)}_{\mathrm{CCSD}}=\frac{2n}{K}\sum_{i,a}\;\sum_{k_i\in\mathbb{K}_n}f^{ik_i}_{ak_a}t^{ak_a}_{ik_i}+\frac{n^2}{K}\sum_{i,j,a,b}\;\sum_{k_i,k_j\in\mathbb{K}_n}\tilde{w}^{ik_ijk_j}_{ak_abk_b}t^{ak_a}_{ik_i}t^{bk_b}_{jk_j}+\frac{n^3}{K}\sum_{i,j,a,b}\;\sum_{k_i,k_j,k_a\in\mathbb{K}_n}\tilde{w}^{ik_ijk_j}_{ak_abk_b}t^{ak_abk_b}_{ik_ijk_j}, \tag{13}$$

respectively, where

$$\tilde{v}^{ik_ijk_j}_{ak_abk_b}=\frac{1}{K}\sum_{\kappa,\lambda,\mu,\nu}\;\sum_{m_1=-S}^{+S}\;\sum_{m_2=-K/(2n)}^{+K/(2n)}\;\sum_{m_3=m_2-S}^{m_2+S}c^{\kappa k_i*}_{ik_i}c^{\lambda k_a}_{ak_a}c^{\mu k_j*}_{jk_j}c^{\nu k_b}_{bk_b}\exp\{i(m_1k_a-m_2k_j+m_3k_b)a\}v^{\kappa(0)\mu(m_2)}_{\lambda(m_1)\nu(m_3)} \tag{14}$$

and $\tilde{w}^{ik_ijk_j}_{ak_abk_b}=2\tilde{v}^{ik_ijk_j}_{ak_abk_b}-\tilde{v}^{ik_ijk_j}_{bk_bak_a}$. Note the reduction in the long-range cutoff in Eq. (14). The costs of evaluating Eqs. (12) and (13) are only n^{-4} and n^{-3} of those of evaluating the corresponding original equations.

The t-amplitude equations, Eqs. (9) and (10), are also adjusted accordingly by systematically making the replacement,

$$\sum_{k_p}\mapsto n\sum_{k_p\in\mathbb{K}_n}. \tag{15}$$

Each such replacement contributes to an n-fold reduction in the cost of the summation. Overall, therefore, the solution of the t-amplitude equations is accelerated by a factor of n^4 by the mod-n scheme.

The presence of the weights such as n^4 in Eq. (12) distinguishes the mod-n scheme from other orbital compression schemes (for example, Ref. 12) that discard orbitals but do not compensate for the neglected contributions. These weights indeed allow as much as 80% of orbitals to be unsampled and nearly (sometimes more than) 100% of the correlation energies to be recovered.

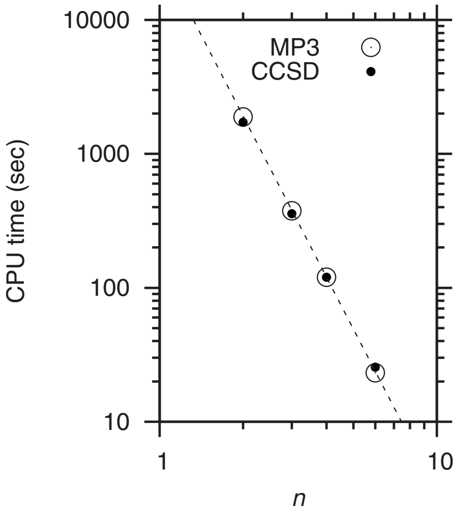

FIG. 1. The CPU time spent by mod-n MP3 and CCSD (one iteration) for polyethylene (K=24 and the STO-3G basis set) as a function of n on a 3.2-GHz Intel Xeon EM64T processor with a 4-GB RAM. The dashed line represents the n^{-4} dependence.

The mod-n scheme can be justified for insulators and semiconductors on a rigorous physical basis.[8–10] Note that the correlation interaction summed in MP3 and CCSD energies decay much more rapidly with distance (as r^{-6} at the slowest) than does the Coulomb (J) interaction in the HF energy (decaying as r^{-3} at the slowest). Since K corresponds to the number of unit cells under the periodic boundary conditions,[13] it needs to be as great as twice the number of the nearest-neighbor unit cells the interaction reaches. The value of K in the MP3 and CCSD step, therefore, can be much smaller than that for the HF step. This also requires that the real-space lattice sums be truncated in a smaller radius as in Eq. (14). This argument can be viewed as an application of Shannon's sampling theorem.[14] This physical basis is the near sightedness of correlation in the words of Kohn[15] and is the same as that underlies local-basis, linear-scaling algorithms such as the Wannier-orbital-based method of Förner *et al.*,[16] the AO-based method of Ayala *et al.*,[17] and

TABLE I. The electron correlation energies (in E_h) of polyethylene obtained by the mod-n MP2, MP3, and CCSD method with the STO-3G basis set and K=24. The breakdown of the CCSD correlation energies into the mth nearest C_2H_4 unit-cell contributions is also shown. The B3LYP/6-31G* geometry of Ref. 21 was used.

n	2	3	4	6
$E^{(n)}_{\mathrm{MP2}}$	−0.10320	−0.10324	−0.10330	−0.10349
$E^{(n)}_{\mathrm{MP3}}$	−0.02282	−0.02280	−0.02277	−0.02268
$E^{(n)}_{\mathrm{CCSD}}$	−0.13574	−0.13576	−0.13580	−0.13594
$m=0$	−0.13419	−0.13419	−0.13420	−0.13431
$m=1$	−0.00154	−0.00155	−0.00158	−0.00147
$m=2$	0.00001	0.00000	0.00007	−0.00016
$m=3$	−0.00001	0.00002	−0.00010	
$m=4$	−0.00001	−0.00005		
$m=5$	0.00001			
$m=6$	−0.00002			

TABLE II. Harmonic (HRM) and anharmonic (VCI) frequencies (in cm^{-1}) of the infrared- or Raman-active vibrations in polyethylene obtained with multiresolution 3MR PESs computed by mod-n MP2/6-31G* for V_1 and HF/6-31G* for V_2+V_3 with $K=20$.

	$n=1$ (Ref. 22)		$n=5$		$n=10$		
Mode	HRM[a]	VCI	HRM[a]	VCI	HRM[a]	VCI	Obs. (Refs. 27 and 28)
$\nu_6(\pi)$	3244	3000	3244	2998	3239	2989	2920
$\nu_6(0)$	3204	2964	3204	2962	3197	2954	2881
$\nu_1(\pi)$	3177	2929	3177	2927	3174	2922	2850
$\nu_1(0)$	3164	2925	3163	2924	3157	2864	2846
$\nu_2(\pi)$	1566	1528	1566	1528	1562	1522	1475
$\nu_2(0)$	1543	1494	1542	1493	1535	1477	1442
$\nu_3(\pi)$	1430	1421	1430	1422	1426	1452	1412
$\nu_7(\pi)$	1337	1317	1338	1317	1339	1318	1295
$\nu_3(0)$	1201	1205	1201	1204	1198	1202	1173
$\nu_7(0)$	1235	1221	1234	1220	1221	1208	1172
$\nu_4(0)$	1180	1163	1180	1162	1164	1145	1134
$\nu_4(\pi)$	1107	1099	1108	1100	1098	1123	1062
$\nu_8(0)$	1071	1080	1070	1080	1070	1080	1050
$\nu_8(\pi)$	693	752	691	751	662	734	722
max[b]	327	83	327	81	324	73	
mad[b]	127	47	127	47	123	40	

[a] Approximate values (see text).

[b] The maximum and mean absolute deviations from the observed.

the divide-and-conquer method of Kobayashi *et al.*[18–20]

Conversely, the mod-n scheme cannot be justified for metals, in which correlation interactions do not decay so rapidly. For systems with vanishing band gaps, the MP2 and MP3 energies are divergent and even HF and CCSD may be inadequate with and without the mod-n approximation. However, there should be no difficulty in applying the mod-n scheme to two- and three-dimensional insulators and semiconductors.

Equations (5) and (6) indicate that elements of f scale as K^0 whereas elements of v and w display K^{-1} dependence. Remembering that each fourfold k summation in Eq. (1) contributes a factor of K^4, one can infer that E_{MP3} is a K^0 quantity and is, therefore, size intensive. If one assumes that t_1, κ, and λ scale as K^0 and t_2 and χ as K^{-1}, one can show that E_{CCSD} is size intensive. It can be readily verified that Eqs. (9) and (10) exhibit consistent K dependence under this same assumption, proving the size extensivity of CCSD. The substitutions of Eq. (15) do not alter this conclusion.

One example of the mod-n approximation is the Γ approximation obtained by setting $n=K$.[8] It takes into account only the $k=0$ (Γ-point) contributions in the lattice summations. It also amounts to the effective value of K being unity and, therefore, makes any correlation method size extensive because quantities in its formulation can no longer depend on K or display inconsistent K dependence. We do not consider this approximation for MP3 or CCSD but use it in anharmonic vibrational treatments (see below).

III. RESULTS AND DISCUSSION

All calculations were performed on polyethylene using the frozen core approximation and $S=6$ and $L=10$ as the short- and long-range cutoff parameters of the lattice summations.

Figure 1 plots the CPU time spent by the mod-n MP3 and CCSD calculations with $n=2$, 3, 4, or 6 and $K=24$. The observed speedup nearly exactly agrees with the theoretical value of n^4. The mod-6 scheme, therefore, is estimated to achieve the incredible 1300-fold speedup relative to the conventional ($n=1$) calculation, which has not been feasible because of too great a storage requirement. The mod-n scheme reduces the latter by a factor of n^3 or 216 at $n=6$.

Table I compares the correlation energies obtained by the mod-n MP2, MP3, and CCSD methods. The errors introduced by the mod-n scheme (as judged by the comparison with the mod-2 results) are no more than a few tenths of 1 mE_{h} or a few tenths of 1% of the total correlation energy in all cases, which are tolerable in view of the enormous speedup. The observed errors in mod-n MP3 and CCSD for polyacetylene (not shown) are somewhat greater than those in polyethylene and we thus place the typical errors of these methods to be a few percent of total correlation energies.

The breakdown of the CCSD correlation energy into unit-cell contributions was obtained by the procedure described in Ref. 2. Approximately 99% of the correlation energy comes from the central unit cell ($m=0$). The first nearest-neighbor cell ($m=1$) accounts for the vast majority of the remainder. This rapid decay of correlation interactions with distance in this insulator justifies essentially the second-nearest-neighbor approximation, to which the mod-6 scheme corresponds. The magnitudes of the one-electron integrals also drop to less than 4% of the intracell values in the second-nearest-neighbor cell.

TABLE III. Harmonic (HRM) and anharmonic (VCI) frequencies (in cm^{-1}) of the infrared- or Raman-active vibrations in polyethylene obtained with multiresolution 3MR PESs computed by mod-5 MP2/6-31G*, MP3/6-31G*, or CCSD/6-31G* for V_1 and HF/6-31G* for V_2+V_3 with $K=20$.

	MP2		MP3		CCSD		
Mode	HRM[a]	VCI	HRM[a]	VCI	HRM[a]	VCI	Obs. (Refs. 27 and 28)
$\nu_6(\pi)$	3244	2998	3235	2991	3224	2957	2920
$\nu_6(0)$	3204	2962	3193	2957	3182	2926	2881
$\nu_1(\pi)$	3177	2927	3175	2928	3164	2896	2850
$\nu_1(0)$	3163	2924	3163	2864	3154	2840	2846
$\nu_2(\pi)$	1566	1528	1568	1531	1557	1520	1475
$\nu_2(0)$	1542	1493	1545	1495	1534	1486	1442
$\nu_3(\pi)$	1430	1422	1446	1450	1433	1444	1412
$\nu_7(\pi)$	1338	1317	1341	1319	1331	1312	1295
$\nu_3(0)$	1201	1204	1206	1210	1197	1205	1173
$\nu_7(0)$	1234	1220	1239	1224	1231	1218	1172
$\nu_4(0)$	1180	1162	1186	1167	1183	1163	1134
$\nu_4(\pi)$	1108	1100	1109	1103	1102	1101	1062
$\nu_8(0)$	1070	1080	1075	1083	1081	1078	1050
$\nu_8(\pi)$	691	751	691	750	735	747	722
max[b]	327	81	325	78	314	46	
mad[b]	127	47	129	46	121	34	

[a] Approximate values (see text).

[b] The maximum and mean absolute deviations from the observed.

How accurately does the mod-n scheme reproduce relative energies? Previously, we examined this question by comparing MP2 quasiparticle energies with and without the mod-n scheme[8,9] and concluded that the scheme remains reliable for relative energies. In this work, we address this by applying mod-n MP2, MP3, and CCSD to the PES of polyethylene in harmonic and anharmonic frequency calculations of its infrared- and Raman-active ($k=0$) vibrations.

The vibrational Schrödinger equation of polyethylene was solved[22] by vibrational configuration interaction (VCI) in the Γ approximation[8] as implemented in SINDO.[23] As stated earlier, the Γ approximation is the mod-n scheme with $n=K$. In this limit, any vibrational method—even VCI—becomes size extensive.[22] It can only yield the energies of in-phase ($k=0$) vibrations, which are, however, the ones observable by infrared and Raman spectroscopies. The force constants needed for these calculations are those with respect to in-phase normal coordinates, which can be obtained by the CO calculations adopting the most compact unit cells, namely, without the supercell or frozen phonon approach.

The PES was approximated by a quartic force field[24] in the three-mode coupling (3MR) approximation.[25] Its intrinsic one-, two-, and three-mode coupling contributions (V_1, V_2, and V_3, respectively) were computed by different electronic structure methods:[26] V_1 by mod-n MP2, MP3, or CCSD and V_2 and V_3 by HF, all with the 6-31G* basis set. The vibrational self-consistent field (VSCF) calculations in the Γ approximation were performed initially on the zero-point state, employing the 11 lowest-lying harmonic-oscillator wave functions along each $k=0$ normal mode. The VCI problems (again in the Γ approximation) were then solved using the VSCF states as the basis set, where up to quadruple excitations were included with the maximum sums of quantum numbers restricted to 5. The convergence of the frequencies was verified by increasing these parameters. Harmonic frequencies were also obtained, albeit approximately, by zeroing cubic and quartic force constants. Further details such as the geometry and normal modes used can be found in Ref. 22.

Table II compares the harmonic and anharmonic frequencies of polyethylene obtained, at least partly, by mod-n MP2 with $n=1$, 5, or 10 and $K=20$. The frequencies obtained with $n=5$ do not differ from those without the mod-n approximation ($n=1$) (Ref. 22) more than 2 cm^{-1}. This attests to the fact that the errors incurred by the mod-5 scheme in the shape of the PES are negligible. The mod-10 scheme causes slightly greater errors, which are still surprisingly small considering that the effective value of K is only two. On the basis of this comparison, we elect to use the mod-5 scheme for the rest of the calculations.

Table III compiles the results obtained with the mod-5 MP2, MP3, and CCSD calculations for V_1 and the HF calculations for V_2 and V_3. In view of the comparison in Table II, we expect the MP3 and CCSD frequencies in Table III to be within a few reciprocal centimeter of the corresponding values without the mod-n scheme, which would cost, if feasible, estimated 625 times as much CPU time and 125 times as much disk space as the mod-5 calculations.

As the level of electron-correlation theory is increased from MP2 to MP3 and CCSD, the harmonic frequencies do not improve substantively and the errors from the observed[27,28] remain greater than 300 (maximum) and 120 (mean) cm^{-1}. The inclusion of the effect of anharmonicity by VCI reduces the maximum and mean absolute deviations by factors of 4–7 and 3, respectively. The calculated anharmonic frequencies, on the other hand, systematically approach the observed as the theoretical level is raised. The anharmonic frequencies of CCSD are within only 46 cm^{-1} of the observed without empirical scaling of force constants or harmonic frequencies.

IV. CONCLUSION

This paper has reported an *ab initio* correlated treatment of both electronic and vibrational degrees of freedom in extended systems of one-dimensional periodicity. Electron correlation has been described, at least partly, by CCSD, whereas vibrational correlation (anharmonicity) by VCI. The mod-*n* approximation has been crucial in making the electronic part of the calculation feasible by reducing the operation and storage cost by three and two orders of magnitude, respectively, relative to the conventional calculation. The Γ approximation, which is a special case of the mod-*n* scheme, has rendered the VCI treatment size extensive and applicable to extended systems.

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[1] S. Hirata, I. Grabowski, M. Tobita, and R. J. Bartlett, Chem. Phys. Lett. **345**, 475 (2001).

[2] S. Hirata, R. Podeszwa, M. Tobita, and R. J. Bartlett, J. Chem. Phys. **120**, 2581 (2004).

[3] A. B. Kunz, Phys. Rev. B **6**, 606 (1972).

[4] S. Suhai, Phys. Rev. B **27**, 3506 (1983).

[5] S. Suhai, Int. J. Quantum Chem. **S48**, 131 (1993).

[6] S. Suhai, Phys. Rev. B **50**, 14791 (1994).

[7] J.-Q. Sun and R. J. Bartlett, Phys. Rev. Lett. **77**, 3669 (1996).

[8] T. Shimazaki and S. Hirata, Int. J. Quantum Chem. **109**, 2953 (2009).

[9] S. Hirata and T. Shimazaki, Phys. Rev. B **80**, 085118 (2009).

[10] Y.-Y. Ohnishi and S. Hirata, J. Chem. Phys. **133**, 034106 (2010).

[11] J. Delhalle, L. Piela, J. L. Brédas, and J.-M. André, Phys. Rev. B **22**, 6254 (1980).

[12] A. G. Taube and R. J. Bartlett, Collect. Czech. Chem. Commun. **70**, 837 (2005).

[13] S. Hirata, Phys. Chem. Chem. Phys. **11**, 8397 (2009).

[14] C. E. Shannon, Proc. IRE **37**, 10 (1949).

[15] W. Kohn, Int. J. Quantum Chem. **56**, 229 (1995).

[16] W. Förner, R. Knab, J. Čížek, and J. Ladik, J. Chem. Phys. **106**, 10248 (1997).

[17] P. Y. Ayala, K. N. Kudin, and G. E. Scuseria, J. Chem. Phys. **115**, 9698 (2001).

[18] M. Kobayashi, T. Akama, and H. Nakai, J. Chem. Phys. **125**, 204106 (2006).

[19] M. Kobayashi, Y. Imamura, and H. Nakai, J. Chem. Phys. **127**, 074103 (2007).

[20] M. Kobayashi and H. Nakai, J. Chem. Phys. **129**, 044103 (2008).

[21] S. Hirata and S. Iwata, J. Chem. Phys. **108**, 7901 (1998).

[22] M. Keçeli, S. Hirata, and K. Yagi, J. Chem. Phys. **133**, 034110 (2010).

[23] K. Yagi, SINDO (2006).

[24] K. Yagi, K. Hirao, T. Taketsugu, M. W. Schmidt, and M. S. Gordon, J. Chem. Phys. **121**, 1383 (2004).

[25] S. Carter, S. J. Culik, and J. M. Bowman, J. Chem. Phys. **107**, 10458 (1997).

[26] K. Yagi, S. Hirata, and K. Hirao, Theor. Chem. Acc. **118**, 681 (2007).

[27] Y. Takahashi, Macromolecules **34**, 7836 (2001).

[28] Y. Takahashi, Macromolecules **38**, 5356 (2005).