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Highly accurate treatment of electron correlation in polymers: coupled-cluster and many-body perturbation theories

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Abstract

A series of accurate and size-extensive ab initio wavefunction-based methods, i.e., coupled-cluster (CCD, CCSD, LCCD, ACCD, QCISD, and LCCSD) and many-body perturbation theories [MBPT(2) and MBPT(3)], are formulated and implemented for infinitely extended one-dimensional lattices (polymers), by taking account of the periodic boundary conditions. We present the results of initial benchmark calculations and also investigate the spatial spread of electron correlation by plotting the atomic-orbital-based t_1 - and t_2 -amplitudes with respect to a unit cell parameter n . The two-electron integrals and t_2 -amplitudes decay as n^{-1} and n^{-3} , leading to the n^{-3} convergence of the lattice summations for correlation energies. © 2001 Published by Elsevier Science B.V.

1. Introduction

Recently, a considerable amount of effort has been devoted to making accurate and size-extensive ab initio wavefunction-based methods, such as coupled-cluster (CC) [1] and many-body perturbation theories (MBPT) [2], feasible for huge or infinitely extended systems. The underlying idea of these fast CC/MBPT methods (see, e.g., [3,4]) is that, in the words of Kohn [5], electron correlation is nearsighted. Hence the computation and storage of molecular integrals and of other intermediate quantities involving two or more separate units of

the system which are far apart from each other can be avoided without compromising the accuracy of the calculations. For infinitely extended periodic systems, the prescreening of molecular integrals and of other quantities can be accomplished by truncating the lattice summations in a well-balanced manner [6]. By grouping long-range repulsive and attractive interactions that largely cancel with each other and approximating them by multipole expansion techniques [6], one can perform a reliable ab initio linear-combination-of-atomic-orbital (LCAO) crystalline orbital (CO) calculation [7,8] of an insulator or a semi-conductor in its ground [6] or excited [9] electronic state by computing the symmetrically unique molecular integrals that extend just over several neighbor unit cells.

Nevertheless, electron correlation imposes severe additional constraints on periodic wavefunc-

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tion calculations. Previous attempts to include the effect of electron correlation in ab initio CO calculations have been made by Suhai [10–14], who considered MBPT through fourth order for extended systems (see also [15–17]). Subsequently, Förner and coworkers [18] formulated and implemented CC doubles (CCD) [19,20] and linearized CCD (LCCD). Reinhardt [21] developed coupled-electron-pair approximations (CEPA) for extended systems from a dressed-configuration-interaction viewpoint, and Dolg and coworkers [22,23] demonstrated the effectiveness of the so-called incremental approach to CC, which replaces the periodic boundary condition problem by that for the usual molecular clusters. Recently, Sun and Bartlett [24,25] performed thorough formal and computational analyses of periodic MBPT(2) correlation and quasiparticle energies, while Hirata and Iwata [26] developed an analytical gradient scheme for the same method. Undoubtedly, this highly accurate and systematically improving series of ab initio wavefunction methods, now well established in the field of quantum chemistry, will offer significant insights into the foremost problems of solid state physics, such as band gaps, phonon spectra, optical and magnetic properties, and superconductivity, with the aid of increasingly powerful algorithms and computers, if they can be applied successfully for such systems [27].

In this Letter, we formulate and implement CC with single and double substitution operators (CCSD) [28] employing the complex canonical Hartree–Fock (HF) Bloch orbitals of infinitely extended one-dimensional lattices (polymers) for the first time. Besides CCSD, we consider its approximations, linearized CCSD (LCCSD), quadratic configuration interaction with single and double substitution operators (QCISD) [29], approximate CCD (ACCD) [30,31], CCD, LCCD, MBPT(2), and MBPT(3). We present the results of benchmark calculations for an infinite linear chain of lithium hydride units $[(\text{LiH})_n]$ and also investigate the spatial spread of electron correlation by plotting the AO-based CC excitation amplitudes (t -amplitudes) [4] with respect to a unit cell parameter. The present study, therefore, raises the prospect that a converging series of approximations analogous to the molecular paradigm,

$$\begin{aligned} \text{HF} < \text{MBPT}(2) &\approx \overline{\text{MBPT}}(3) < \text{CCD} < \text{CCSD} \\ &\approx \text{MBPT}(4) < \text{CCSD}(T) \\ &< \text{CCSDT} < \text{full CI} \end{aligned}$$

(cf. [32]), can be envisioned for extended systems.

2. Theory

The CC method uses an exponential wavefunction Ψ written as

$$\Psi = \exp(T)\Phi_{\text{HF}} = \sum_{n=0}^N T^n/n!\Phi_{\text{HF}}, \quad (1)$$

where Φ_{HF} is a reference HF determinant [7,8] constructed from N occupied canonical HF Bloch spinorbitals. For CCSD, the cluster operator T is a sum of single excitations T_1 and double excitations T_2 defined by

$$T_1 = \sum_i^{\text{occ.}} \sum_a^{\text{virt.}} t_{ik_i}^{ak_a} a_{ak_a}^\dagger a_{ik_i}, \quad (2a)$$

$$T_2 = (2!)^{-2} \sum_{ij}^{\text{occ.}} \sum_{ab}^{\text{virt.}} t_{ik_jk_a}^{ak_a bk_b} a_{ak_a}^\dagger a_{ik_i} a_{bk_b}^\dagger a_{jk_j}. \quad (2b)$$

Notice that not all the wavevector indices are varied independently of each other in the summations, because, owing to the periodicity, the excitation amplitudes (t -amplitudes) vanish when such excitations do not conserve momentum. Specifically, we need to consider only the t_1 - and t_2 -amplitudes whose corresponding wavevectors fulfill the conditions:

$$(\mathbf{k}_a - \mathbf{k}_i) \cdot \mathbf{a} = 2\pi m, \quad (3a)$$

$$(\mathbf{k}_a + \mathbf{k}_b - \mathbf{k}_i - \mathbf{k}_j) \cdot \mathbf{a} = 2\pi n, \quad (3b)$$

respectively, where \mathbf{a} is the fundamental vector that outlines the unit cell and m and n are integers. The t -amplitudes and correlation energy per unit cell ΔE_{CC} are determined by

$$\langle \Phi_{\text{HF}} | [H_{\text{N}} \exp(T)]_{\text{C}} | \Phi_{\text{HF}} \rangle = K \Delta E_{\text{CC}}, \quad (4a)$$

$$\langle \Phi_{ik_i}^{ak_a} | [H_{\text{N}} \exp(T)]_{\text{C}} | \Phi_{\text{HF}} \rangle = 0 \quad (\forall iak_i), \quad (4b)$$

$$\langle \Phi_{ik_jk_a}^{ak_a bk_b} | [H_{\text{N}} \exp(T)]_{\text{C}} | \Phi_{\text{HF}} \rangle = 0 \quad (\forall ijabk_i k_j k_a), \quad (4c)$$

etc., where K is the number of wavevector sampling points, $H_N = H - \langle \Phi_{\text{HF}} | H | \Phi_{\text{HF}} \rangle$, and the subscript C means that all terms in the second quantized form of H_N and T must be connected by common indices [1]. The projection equations onto the determinants which do not have the same momentum as Φ_{HF} need not be considered.

The projection equations derive the energy expression and amplitude equations, most expediently by diagrammatic approaches [1] supplemented with the additional rules that arise from the periodic boundary conditions. The closed-

shell [1,28,33] CCSD energy expressions and amplitude equations are given in Table 1, in which I, J, K, L denote the composite indices of occupied bands and wavevectors (ik_i, jk_j, k_k, lk_l , respectively) and A, B, C, D the composite indices of virtual bands and wavevectors, f_Q^P a CO-based Fock matrix element, v_{RS}^{PQ} a CO-based two-electron integral, and $w_{RS}^{\text{PQ}} = 2v_{RS}^{\text{PQ}} - v_{SR}^{\text{PQ}}$. Owing to the periodicity, $f_Q^P, \kappa_Q^P, \lambda_Q^P, v_{RS}^{\text{PQ}}, w_{RS}^{\text{PQ}}$, and χ_{RS}^{PQ} vanish unless momentum conservation conditions analogous to Eq. (3) are fulfilled.

Table 1
Closed-shell CCSD energy expression and amplitude equations for extended systems

$$\begin{aligned} \Delta E_{\text{CCSD}} &= 2K^{-1} \sum_{ia} \sum_{k_l} f_{A_i}^l t_l^A + K^{-1} \sum_{ijab} \sum_{k_l k_j} w_{AB}^{ij} t_l^A t_j^B + K^{-1} \sum_{ijab} \sum_{k_l k_j k_a} w_{AB}^{ij} t_l^A t_j^B \\ 0 &= f_I^A - 2 \sum_{kc} f_C^K t_k^A t_l^C + \sum_c \kappa_C^A t_l^C - \sum_k \kappa_I^K t_k^A + \sum_{kc} \sum_{k_k} \kappa_C^K (2t_{kI}^{cA} - t_{IK}^{cA}) + \sum_{kc} \kappa_C^K t_l^C t_k^A + \sum_{kc} \sum_{k_k} w_{IC}^{AK} t_l^C + \sum_{kcd} \sum_{k_k k_c} w_{CD}^{AK} t_l^C t_k^D + \sum_{kcd} \sum_{k_k} w_{CD}^{AK} t_l^C t_k^D \\ &\quad - \sum_{klc} \sum_{k_k k_l} w_{IC}^{KL} t_{kL}^A t_l^C - \sum_{klc} \sum_{k_l} w_{IC}^{KL} t_k^A t_l^C \\ 0 &= v_{AB}^{J*} + \sum_{kl} \sum_{k_k} \chi_{IJ}^{KL} t_{kL}^{AB} + \sum_{kl} \sum_{k_l} \chi_{IJ}^{KL} t_{kL}^A t_l^B + \sum_{cd} \sum_{k_c} \chi_{CD}^{AB} t_l^C t_j^D + \sum_{cd} \chi_{CD}^{AB} t_l^C t_j^D + P \sum_c \chi_c^A t_{IJ}^{CB} - P \sum_k \chi_k^A t_{IJ}^{AB} + P \sum_c \left(v_{IC}^{AB} - \sum_k v_{IC}^{KB} t_k^A \right) t_l^C - P \\ &\quad \times \sum_k \left(v_{IJ}^{AK} + \sum_c v_{IC}^{AK} t_l^C \right) t_k^B + P \sum_{kc} \sum_{k_k} (2\chi_{IC}^{AK} - \chi_{CI}^{AK}) t_{kI}^{CB} - P \sum_{kc} \sum_{k_k} \chi_{IC}^{AK} t_{kI}^{BC} - P \sum_{kc} \sum_{k_k} \chi_{CI}^{BK} t_{kI}^{AC} \\ \kappa_I^K &= f_I^K + \sum_{lcd} \sum_{k_l k_c} w_{CD}^{KL} t_{lL}^C t_l^D + \sum_{lcd} \sum_{k_l} w_{CD}^{KL} t_l^C t_l^D \\ \kappa_C^A &= f_C^A - \sum_{kld} \sum_{k_k k_l} w_{CD}^{KL} t_{kL}^A t_l^D - \sum_{kld} \sum_{k_l} w_{CD}^{KL} t_k^A t_l^D \\ \kappa_C^K &= f_C^K + \sum_{ld} \sum_{k_l} w_{CD}^{KL} t_l^D, \\ \lambda_I^K &= \kappa_I^K + \sum_c f_C^K t_l^C + \sum_{lc} \sum_{k_l} w_{IC}^{KL} t_l^C \\ \lambda_C^A &= \kappa_C^A - \sum_k f_C^K t_k^A + \sum_{kd} \sum_{k_k} w_{CD}^{AK} t_k^D \\ \chi_{IJ}^{KL} &= v_{IJ}^{KL} + \sum_c v_{IC}^{KL} t_l^C + \sum_c v_{CJ}^{KL} t_l^C + \sum_{cd} \sum_{k_c} v_{CD}^{KL} t_l^C t_j^D + \sum_{cd} v_{CD}^{KL} t_l^C t_j^D \\ \chi_{CD}^{AB} &= v_{CD}^{AB} - \sum_k v_{CD}^{AK} t_k^B - \sum_k v_{CD}^{KB} t_k^A \\ \chi_{IC}^{AK} &= v_{IC}^{AK} - \sum_l v_{IC}^{LK} t_l^A + \sum_d v_{DC}^{AK} t_l^D - 1/2 \sum_{ld} \sum_{k_l} v_{DC}^{LK} t_{lL}^{DA} - \sum_{ld} v_{DC}^{LK} t_l^D t_l^A + 1/2 \sum_{ld} \sum_{k_l} w_{DC}^{LK} t_{lL}^{AD} \\ \chi_{CI}^{AK} &= v_{CI}^{AK} - \sum_l v_{CI}^{LK} t_l^A + \sum_d v_{CD}^{AK} t_l^D - 1/2 \sum_{ld} \sum_{k_l} v_{CD}^{LK} t_{lL}^{DA} - \sum_{ld} v_{CD}^{LK} t_l^D t_l^A \\ P\{\dots\}_{IJ}^{AB} &= \{\dots\}_{IJ}^{AB} + \{\dots\}_{JI}^{BA} \end{aligned}$$

Table 2

Closed-shell MBPT(2) and MBPT(3) energy expressions for extended systems

$$E^{(2)} = K^{-1} \sum_{ijab} \sum_{k_i k_j k_a} (D_{AB}^{JJ})^{-1} v_{AB}^{JJ} w_{AB}^{JJ*}$$

$$E^{(3)} = K^{-1} \sum_{ijabcd} \sum_{k_i k_j k_a k_c} (D_{AB}^{JJ})^{-1} (D_{CD}^{JJ})^{-1} v_{AB}^{JJ} v_{CD}^{AB} w_{CD}^{JJ*} + K^{-1} \sum_{ijklab} \sum_{k_i k_j k_k k_a} (D_{AB}^{JJ})^{-1} (D_{AB}^{KL})^{-1} v_{AB}^{JJ} v_{IJ}^{KL} w_{AB}^{KL*}$$

$$+ 4K^{-1} \sum_{ijkabc} \sum_{k_i k_j k_a k_c} (D_{AB}^{JJ})^{-1} (D_{AC}^{JK})^{-1} v_{AB}^{JJ} v_{CJ}^{KB} w_{AC}^{JK*} - 2K^{-1} \sum_{ijkabc} \sum_{k_i k_j k_a k_c} (D_{AB}^{JJ})^{-1} (D_{BC}^{JK})^{-1} v_{AB}^{JJ} v_{IC}^{KA} w_{BC}^{JK*}$$

$$- 2K^{-1} \sum_{ijkabc} \sum_{k_i k_j k_a k_c} (D_{AB}^{JJ})^{-1} (D_{BC}^{JK})^{-1} v_{AB}^{JJ} w_{JC}^{KA} v_{CB}^{JK*} - 2K^{-1} \sum_{ijkabc} \sum_{k_i k_j k_a k_c} (D_{AB}^{JJ})^{-1} (D_{AC}^{JK})^{-1} v_{AB}^{JJ} w_{CI}^{KB} v_{AC}^{JK*}$$

$$D_{AB}^{JJ} = \epsilon_I + \epsilon_J - \epsilon_A - \epsilon_B$$

From Rayleigh–Schrodinger perturbation theory employing the Møller–Plesset partitioning of H , the total energy per unit cell E can be expanded as

$$E = E_{\text{HF}} + E^{(2)} + E^{(3)} + \dots \quad (5)$$

The explicit expressions of $E^{(2)}$ and $E^{(3)}$ are given in Table 2, in which ϵ_p is the energy of a one-particle state in energy band p with wavevector \mathbf{k}_p .

3. Demonstrative calculations

The CC/MBPT methods are implemented in the POLYMER quantum chemistry computer code [34]. CO-based two-electron integrals, the intermediates $\{\chi_{\text{RS}}^{\text{PQ}}\}$, and t_2 -amplitudes are stored externally in direct access files addressed by sets of three wavevector indices $(\mathbf{k}_p, \mathbf{k}_q, \mathbf{k}_r)$. The DIIS/RLE extrapolation [35] is invoked to accelerate the iterative procedure for solving the amplitude equations. In our implementation, disk space size, memory size, and cpu time required for a CCSD calculation roughly scale as $\mathcal{O}(n^4 K^3)$, $\mathcal{O}(n^4 K)$, and $\mathcal{O}(n^6 K^4)$, respectively, where n is the number of energy bands.

The results of benchmark CC/MBPT calculations of $(\text{LiH})_x$ [6] are presented in Table 3. We truncate the short- and long-range lattice summations after five neighbors on both sides of the reference cell and sample 10 evenly spaced wavevectors in the first Brillouin zone, providing the energies at a precision of $10^{-5} E_{\text{H}}$ or better. The multipole expansion corrections to the Fock ma-

Table 3

Total (E) and correlation energies ($E_{\text{corr.}}$) (in E_{H}) of an infinite linear chain of LiH $[(\text{LiH})_x]$ with the Li–H and H–Li distances being 4.0 and 6.0 a.u.

Theory	E	$E_{\text{corr.}}$
HF/6-31G ^a	-7.99282	-
MBPT(2)/6-31G	-8.00567	-0.01285
MBPT(3)/6-31G	-8.00953	-0.01671
LCCD/6-31G	-8.01201	-0.01919
ACCD/6-31G	-8.01158	-0.01876
CCD/6-31G	-8.01157	-0.01875
LCCSD/6-31G	-8.01292	-0.02010
QCISD/6-31G	-8.01235	-0.01952
CCSD/6-31G	-8.01235	-0.01953
HF/6-31G ^{a*}	-7.99368	-
MBPT(2)/6-31G [*]	-8.00856	-0.01488
MBPT(3)/6-31G [*]	-8.01269	-0.01901
LCCD/6-31G [*]	-8.01527	-0.02160
ACCD/6-31G [*]	-8.01476	-0.02109
CCD/6-31G [*]	-8.01476	-0.02108
LCCSD/6-31G [*]	-8.01612	-0.02245
QCISD/6-31G [*]	-8.01546	-0.02179
CCSD/6-31G [*]	-8.01547	-0.02179
HF/6-31G ^{a**}	-7.99372	-
MBPT(2)/6-31G ^{**}	-8.01331	-0.01959
MBPT(3)/6-31G ^{**}	-8.01753	-0.02381
LCCD/6-31G ^{**}	-8.01995	-0.02623
ACCD/6-31G ^{**}	-8.01932	-0.02560
CCD/6-31G ^{**}	-8.01931	-0.02559
LCCSD/6-31G ^{**}	-8.02062	-0.02690
QCISD/6-31G ^{**}	-8.01988	-0.02616
CCSD/6-31G ^{**}	-8.01988	-0.02616

^a Long-range Coulomb interactions are accounted for by a multipole (dipole–dipole and charge–quadrupole) expansion technique.

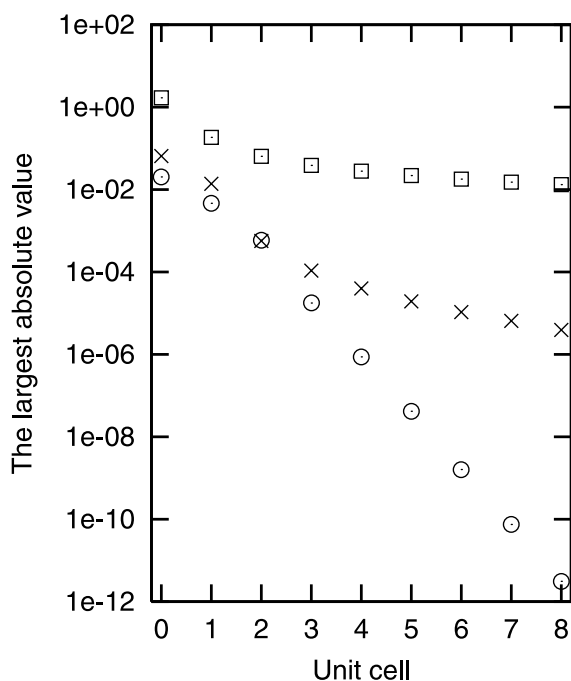


Fig. 1. The largest absolute values of the two-electron integrals (squares) and t_1 - and t_2 -amplitudes (circles and crosses) in the AO basis as a function of the unit cell parameter that approximately measures the distance between the two electrons involved. Obtained from a CCSD/STO-3G calculation of $(\text{LiH})_x$ with 8th (short-range) and 10th (long-range) neighbor approximations and 24 evenly spaced wavevectors in the first Brillouin zone.

trix elements are essential in achieving the precision for correlation energies of $(\text{LiH})_x$, particularly when single substitutions are included in CC (CCSD, QCISD, or LCCSD). In this single $(\text{LiH})_x$ example, it is apparent that some form of an infinite summation of diagrams is requisite to achieve an accuracy of 1–2 $m E_H$ for a given one-particle basis set, since MBPT(3) falls short. However, once the infinite summation is introduced, as in LCCD, there is comparatively little to gain from even higher summations as in CCD and CCSD. This is traced to the electronically localized nature of $(\text{LiH})_x$, and would likely change for more delocalized systems. The extremely accurate agreement between CCD and ACCD might be another manifestation of this localization in $(\text{LiH})_x$, but the latter method, which reduces to CCD for two-electron systems, has certain computational

advantages. It is often said that, because of the infinite nature of the basis set in polymers, there should be a less effect due to polarization functions than in molecular calculations. However, it is apparent that adding the d-type functions to Li (6-31G*) has an effect of 2–3 $m E_H$, while adding the p-type functions to H (6-31G**) has an additional 4–5- $m E_H$ effect.

Fig. 1 plots the largest absolute values of the two-electron integrals and t_1 - and t_2 -amplitudes in the AO basis against the distance (n in units of unit cell) between the two electrons involved. The definition of the AO-based t -amplitudes is based on that of Scuseria and Ayala [4] for finite systems. The AO-based quantities have promise as the basic variables of a fast CC algorithm for extended systems in that only a very small fraction of them have larger absolute values and need to be stored and manipulated. For example, only 4.8 (9.5)% of all t_2 -amplitudes have absolute values greater than 10^{-8} (10^{-10}) in the CCSD/6-31G** calculation of $(\text{LiH})_x$. The t_1 -amplitudes decay much faster (apparently exponentially in this example) than the t_2 -amplitudes and two-electron integrals, the latter dictating the convergence behavior of the lattice summations. The integrals and t_2 -amplitudes decay asymptotically as n^{-1} and n^{-3} , and hence the lattice summations for correlation energies would converge asymptotically as n^{-3} . This is consistent with the earlier proof of Sun and Bartlett [25] that the lattice summations for $E^{(2)}$ converge as n^{-3} . This conclusion would be valid universally for CC/MBPT.

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