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Electron correlation in extended systems: Fourth-order many-body perturbation theory and density-functional methods applied to an infinite chain of hydrogen atoms

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Linear equidistant and bond-alternating infinite chains of hydrogen atoms have been investigated by the *ab initio* crystal-orbital method at the Hartree-Fock (HF) level, by including electron correlation up to the complete fourth order of the Møller-Plesset perturbation theory (MP4-PT), and by using different versions of density-functional theory (DFT). The Bloch functions have been expanded in all cases in a series of high-quality atomic-orbital basis sets and complemented by extended sets of polarization functions up to $6s3p2d1f$ per H atom. In order to compare the performance of the PT and DFT methods, several physical properties have been computed at all theoretical levels including lattice geometry, cohesive energy, mechanisms of bond alternation (Peierls instability), and energetic features of nonequilibrium configurations (dissociation). For this latter quantities, both spin-restricted (RHF) and unrestricted (UHF) wave functions have been employed in all orders of PT. The methods described have been used parallel to infinite chains and to the H_2 molecule, to be able to check their accuracy on experiments. In the case of the DFT, six different functionals (combining Slater and Becke exchange with local and gradient-corrected correlation potentials) have been utilized to test their accuracy in comparison with the MP4 results.

I. INTRODUCTION

Infinite equidistant and bond-alternating linear chains of hydrogen atoms, H_∞ and $(H_2)_\infty$, respectively, provide the most useful model systems in studying electronic structure effects in condensed-matter physics. On the one hand, they frequently serve as the simplest realistic prototypes of quasi-one-dimensional polymeric materials to test various methods for the computation of structural and electronic properties, including the study of electron-electron and electron-lattice interactions, metal-insulator transitions, Peierls instabilities, etc. On the other hand, they provide a zeroth-order model for certain three-dimensional phases of solid metallic hydrogen whose behavior under pressure has been the subject of intensive research both from experimental and theoretical sides (for reviews, see Refs. 1 and 2). It has also been established that electron correlation effects play a predominant role in the physical properties of this material and, therefore, the exact determination of the correlation potential proves to be an outstanding problem for writing down its equation of state.[3] These and related aspects have in the past stimulated, following Slaters original suggestion,[4] a number of theoretical studies on finite hydrogen atom rings and infinite linear chains[5–34] as well as on three-dimensional structures.[35,36] In the case of finite rings, it has been observed[22,23,25] that bond alternation reduces the Hartree-Fock (HF) energy as compared to the case of equidistant rings. On the other hand, correlation contributions turned out to be larger for these latter systems. Furthermore, the bond alternating structures proved to be unstable against the formation of free H_2 molecules.[16] In analogy to other polymers like polyacetylene,[37,38] polysilene,[39] etc., the bond alternation observed at the HF level was somewhat reduced at post-HF levels for $(H_2)_\infty$.[28]

The purpose of the present paper is to investigate four methodological aspects of studying electron correlation effects in extended systems: (i) the performance of different orders of many-body perturbation theory (MBPT); (ii) the choice of restricted and unrestricted zeroth-order Hamiltonians (RHF and UHF, respectively) within the Møller-Plesset (MP) partitioning scheme,[40] (iii) the use of different exchange-correlation potentials of density-functional theory (DFT)[41] and comparison of their results with those of MBPT; and (iv) the inclusion of atomic basis sets of systematically increasing size to be able to extrapolate the results to an "infinite basis set" at all of the above-mentioned theoretical levels. Since various physical properties may be influenced in a different manner by the approximations inherent to each method, we have selected four representative properties of the infinite hydrogen chains to be compared at all levels: (i) the cohesion energy and optimized lattice distance of the equidistant (metallic) chain, (ii) the (uniform) dissociation of the equidistant chain, (iii) the energetics of bond alternation in the dimerized (semiconducting) chain, and (iv) the development of the band gap as function of the dimerization parameter. Section II of the paper will summarize the methodological aspects related to the computation of the correlated ground state of an infinite chain by using the Møller-Plesset partitioning scheme of MBPT and density-functional theory, respectively. Section III contains the results obtained for metallic and semiconducting hydrogen chains at different theoretical levels. Finally, Sec. IV summarizes the conclusions.

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II. CORRELATED GROUND STATE OF EXTENDED SYSTEMS: PERTURBATION THEORY VS DENSITY FUNCTIONALS

Our *ab initio* method of calculating electron correlation effects in extended systems using MBPT techniques has been described in more detail at second,[37,42–45] third,[46] and fourth[47] orders, respectively. Here we provide only a concise summary of the basic expressions to be able to define the various theoretical levels as applied to hydrogen atom chains. Our computational procedure is a generalization of the methods worked out by Pople's group over the past decades[48–50] for molecules, to the case of infinite systems using additional symmetry operations (translation and helical rotation) and different numerical procedures of solid-state theory. During the development of the computer program package POLYGAUSS used in our laboratory for the investigation of the electronic structure of extended systems, we have made intensive use of several techniques and modules of the Gaussian molecular packages starting from Gaussian 76 up to Gaussian 92/DFT.[51] Concerning the DFT part, we also benefited much from experiences gained in using the POLYXA and ADF programs of the Mintmire[25] and Baerends[52] groups, respectively.

In order to introduce the Møller-Plesset (MP) partitioning scheme[40] of the Rayleigh-Schrödinger (RS) MBPT, the full many-electron Hamiltonian $\hat{H}$ will be taken as the Fock Hamiltonian plus a perturbation:

$$\hat{H}=\hat{H}_0+\hat{Q} \ , \tag{1}$$

$$\hat{H}_0=\sum_I \varepsilon_I c_I^\dagger c_I \ , \tag{2}$$

$$\hat{Q}=\tfrac{1}{2}\sum_I \sum_J \sum_L \sum_M \langle IJ|LM\rangle c_I^\dagger c_J^\dagger c_M c_L - \sum_I \sum_J \sum_L \langle LI\|LJ\rangle n_L c_I^\dagger c_J \ . \tag{3}$$

$c_I^\dagger$ and c_I are here creation and annihilation operators, respectively, referring to Hartree-Fock-type Bloch orbitals ϕ_I (the compound index I refers to the band index i and quasimomentum $\mathbf{k}_i$), n_L is the occupation number, and the four-center repulsion integrals are defined by

$$\langle IJ\|LM\rangle=\int d\mathbf{r}_1\int d\mathbf{r}_2 \phi_i^{\mathbf{k}_i}(\mathbf{r}_1)^* \phi_j^{\mathbf{k}_j}(\mathbf{r}_2)^* r_{12}^{-1} \phi_l^{\mathbf{k}_l}(\mathbf{r}_1) \times \phi_m^{\mathbf{k}_m}(\mathbf{r}_2) \ . \tag{4}$$

Integrals of the type $\langle \ldots \| \ldots \rangle$ in Eq. (3) are analogous in their structure to Eq. (4), with the difference that the Coulomb operator is multiplied in them by the factor $(1-\hat{P}_{12})$ to take account of exchange. (The operator $\hat{P}$ interchanges variables $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively, before integration.) The zeroth-order (determinental) many-electron wave functions are eigenfunctions of $\hat{H}_0$:

$$\hat{H}_0\Phi_\lambda=E_\lambda\Phi_\lambda \ . \tag{5}$$

The working expressions of MBPT can be written in a compact form using the reduced resolvent of $\hat{H}_0$ belonging to its lowest eigenvalue, E_0:

$$\hat{G}_0(E_0)=\sum_{\lambda=1}^{\infty}(E_0-E_\lambda)^{-1}|\Phi_\lambda\rangle\langle\Phi_\lambda| \equiv \hat{G} \ . \tag{6}$$

In terms of $\hat{G}$, the first four orders of the RS-MBPT are given by

$$\mathcal{E}^{(1)}=\langle\Phi_0|\hat{Q}|\Phi_0\rangle=\langle\hat{Q}\rangle \ , \tag{7}$$

$$\mathcal{E}^{(2)}=\langle\Phi_0|\hat{Q}\hat{G}\hat{Q}|\Phi_0\rangle \ , \tag{8}$$

$$\mathcal{E}^{(3)}=\langle\Phi_0|\hat{Q}\hat{G}(\hat{Q}-\langle\hat{Q}\rangle)\hat{G}\hat{Q}|\Phi_0\rangle \ , \tag{9}$$

$$\mathcal{E}^{(4)}=\langle\Phi_0|\hat{Q}\hat{G}(\hat{Q}-\langle\hat{Q}\rangle)\hat{G}(\hat{Q}-\langle\hat{Q}\rangle)\hat{G}\hat{Q}|\Phi_{b0}\rangle - \mathcal{E}^{(2)}\langle\Phi_0|\hat{Q}\hat{G}\hat{G}\hat{Q}|\Phi_0\rangle \ . \tag{10}$$

Since $E_{\mathrm{HF}}=\mathcal{E}^{(0)}+\mathcal{E}^{(1)}$, the correlation energy, defined as the difference between the exact eigenvalue of $\hat{H}$ and E_{HF}, can be obtained as the sum of all higher-order terms in the perturbation series starting by $\mathcal{E}^{(2)}$. In order to construct the zeroth-order wave function Φ_0, we have to solve first the HF problem of the crystal. In the case of the spin-restricted RHF theory, the corresponding Fock operator consists of kinetic energy, nuclear contributions, and Coulomb and exchange terms in the form

$$\begin{aligned}\hat{F}(\mathbf{r}_l)&=\hat{T}+\hat{V}+\hat{J}+\hat{K}\\&=-\tfrac{1}{2}\Delta\mathbf{r}_l-\sum_{h=-N_c/2}^{+N_c/2}\sum_{A=1}^{n_A}\frac{Z_A}{|\mathbf{r}_l-\mathbf{R}_h-\mathbf{R}_A|}\\&\quad+\int d^3\mathbf{r}_m\frac{\rho(\mathbf{r}_l,\mathbf{r}_l)}{|\mathbf{r}_l-\mathbf{r}_m|}\\&\quad-\int d^3\mathbf{r}_m\frac{\rho(\mathbf{r}_l,\mathbf{r}_m)}{|\mathbf{r}_l-\mathbf{r}_m|}\hat{P}(\mathbf{r}_l,\mathbf{r}_m) \ ,\end{aligned} \tag{11}$$

where N_c+1 is the number of elementary cells, n_A is the number of atoms per cell, and Z_A is the core charge of the atom A at position $\mathbf{R}_A$. The first-order density matrix $\rho(\mathbf{r}_l,\mathbf{r}_m)$ will be constructed from the (doubly) occupied Bloch spin orbitals by numerical integration over the first Brillouin zone (BZ), and the Bloch orbitals $\phi_n^{\mathbf{k}}(\mathbf{r}_l)$ will be obtained as self-consistent solutions of the Hartree-Fock equations of the crystal.[53,54] For computational purposes, the Bloch functions will be expressed as linear combinations of symmetry-adapted Bloch basis functions, which themselves will be expanded into a set of contracted Gaussian-type atomic orbitals (CGTO's). The N-electron wave function Φ_{HF} will be written as a Slater determinant built from the doubly filled symmetry-adapted Bloch functions. Besides Φ_{HF}, we can construct further eigenfunctions of $\hat{H}_0$ by replacing some of the occupied orbitals in Φ_{HF} by virtual orbitals which we also obtain by solving the eigenvalue problem of $\hat{F}$. Labeling the Bloch states such that indices $I,J,\ldots$ stand for occupied (valence-band) levels in the ground-state configuration, while $A,B,\ldots$ refer to virtual (conduction-band) levels, we can classify the eigenfucntions of $\hat{H}_0$ as single (S), double (D), triple (T), quadruple (Q), etc. excited configurations: $\Phi_I^A=c_A^\dagger c_I\Phi_{\mathrm{HF}}$, $\Phi_{IJ}^{AB}=c_A^\dagger c_B^\dagger c_I c_J\Phi_{\mathrm{HF}}, \ldots$.

As mentioned above, at first order we obtain the term missing from E_0 to the HF energy, i.e.,

$$E_{\mathrm{HF}}=\mathcal{E}^{(0)}+\mathcal{E}^{(1)}=E_0+\langle\Phi_0|\hat{Q}|\Phi_0\rangle\ , \tag{12}$$

while in higher orders we obtain correlation corrections to it. That is, in the fourth order the correlation energy, defined as $E_{\mathrm{corr}}=\mathcal{E}_{\mathrm{exact}}-E_{\mathrm{HF}}$, will be obtained as

$$E_{\mathrm{corr}}=\mathcal{E}^{(2)}+\mathcal{E}^{(3)}+\mathcal{E}^{(4)}\ . \tag{13}$$

Expanding the matrix elements of the perturbation operator between the ground state Φ_0 and doubly excited states (D) of the type $I\rightarrow A, J\rightarrow B$ in the form

$$\begin{aligned}V_{0s}&=\langle\Phi_0|\hat{Q}|\Phi_{IJ}^{AB}\rangle\\&=\int d\mathbf{r}_1\int d\mathbf{r}_2\phi_a^{\mathbf{k}_a}(\mathbf{r}_1)^*\phi_b^{\mathbf{k}_b}(\mathbf{r}_2)^*r_{12}^{-1}[\phi_i^{\mathbf{k}_i}(\mathbf{r}_1)\phi_j^{\mathbf{k}_j}(\mathbf{r}_2)-\phi_j^{\mathbf{k}_j}(\mathbf{r}_1)\phi_i^{\mathbf{k}_i}(\mathbf{r}_2)]\ ,\end{aligned} \tag{14}$$

we obtain the successive energy terms of PT in the form

$$\mathcal{E}^{(2)}=\sum_{s}^{D}(E_0-E_s)^{-1}V_{0s}V_{s0}\ , \tag{15}$$

$$\mathcal{E}^{(3)}=\sum_{st}^{D}(E_0-E_s)^{-1}(E_0-E_t)^{-1}V_{0s}\bar{V}_{st}V_{t0}\ , \tag{16}$$

$$\begin{aligned}\mathcal{E}^{(4)}=&-\sum_{st}^{D}(E_0-E_s)^{-1}(E_0-E_t)^{-2}V_{0s}V_{s0}V_{0t}V_{t0}\\&+\sum_{su}^{D}\sum_{t}^{SDTQ}(E_0-E_s)^{-1}(E_0-E_t)^{-1}(E_0-E_u)^{-1}\\&\qquad\times V_{0s}\bar{V}_{st}\bar{V}_{tu}V_{u0}\ .\end{aligned} \tag{17}$$

In Eqs. (16) and (17), $\bar{V}_{st}=V_{st}-V_{00}\delta_{st}$, and the sums over s, t, and u are over all eigenfunctions of $\hat{H}_0$ except Φ_0. In second order, only matrix elements between the ground state and doubly excited configurations will have to be computed. Starting at third order, however, matrix elements between doubly excited states will also be required. Their list substantially exceeds that of the former elements, since even with the use of basis sets of moderate size the number of virtual bands by far exceeds that of the occupied ones. In fourth order, the sum over t includes all single (S), double (D), triple (T), and quadruple (Q) excitations. For further analysis of different contributions in fourth order, it is convenient to write $\mathcal{E}^{(4)}$ as[50]

$$\mathcal{E}^{(4)}=\mathcal{E}_S^{(4)}+\mathcal{E}_D^{(4)}+\mathcal{E}_T^{(4)}+\mathcal{E}_Q^{(4)}\ , \tag{18}$$

where the first three terms arise from the S, D, and T summations for t in Eq. (17), while $\mathcal{E}_Q^{(4)}$ includes the Q sum and the first sum over D in Eq. (17) (the so-called renormalization term,[49] which provides a partial cancellation of the Q sum). It is important to stress here, in view of applications to infinite systems, that all four parts in Eq. (18) (as well as all terms in lower orders) are individually size consistent, i.e., their application to an array of isolated subunits leads to additive results. Furthermore, in presenting the results it is reasonable to combine the fourth-order contributions from double and quadruple substitutions as $\mathcal{E}_{DQ}^{(4)}$, since $\mathcal{E}_D^{(4)}$ and $\mathcal{E}_Q^{(4)}$ both contain large terms from unlinked clusters that partly cancel each other.[50]

In the case of the spin-unrestricted UHF theory we have to solve the Fock eigenvalue problem simultaneously for both spins, whereby the electron density for α and β spins will be computed analogously to the HF case. The zeroth-order many-electron function for PT will be constructed as $\Phi_{\mathrm{UHF}}=(N!)^{-1/2}\det[\ldots\phi_n^{\mathbf{k},\alpha}(\mathbf{r}_i)\phi_n^{\mathbf{k},\beta}(\mathbf{r}_{i+1})\ldots]$. To compute the correlation terms, we proceed as above using Φ_{UHF} as the reference state. It has to be noted, however, that in this case the wave function Φ_{UHF} itself contains certain amount of correlation due to the definition of E_{corr}. Physically, this correlation energy is the consequence of the use of different spatial orbitals for different spins that introduces a small Coulomb hole into the many-electron system. Though the perturbation theoretical equations have been formulated in the Bloch function basis, in order to make most efficient use of the translational (or helical) symmetry of the system, the transformation from the Bloch basis to that of localized Wannier functions turns out to be a very efficient procedure to actually calculate the matrix elements of $\hat{Q}$ (Refs. 38–42) for semiconductors. For metals, however, the original Bloch formulation of PT has to be used.[24] It has been shown, furthermore, based on $\mathbf{k}\cdot\mathbf{p}$ PT, that in quasi-one-dimensional metallic systems no numerical instabilities should occur around the Fermi level during PT calculations[55] when both the nominator and the denominator approach zero. In order to obtain numerically stable results (especially in the case of large atomic basis sets which frequently lead to numerical problems in solids due to linear dependences[56]), special attention has to be paid to the proper truncation of the lattice sums. The electrostatic terms have been summed up, therefore, in this study to infinity using the multipole expansion technique,[73] while the exchange and correlation terms have been cut off with a radius of 16 Å, ensuring their proper convergence.

Since for higher-order PT the computational costs increase rapidly with the size of the unit cell, there is interest in methods which could reach comparable precision more efficiently. Density-functional theory (DFT) has recently shown promise in this direction.[41] Therefore, it might be useful to compare for our model system PT expansions with different functional forms of DFT to gain some insight into their performance in relation to different physical properties. The Fock operator in this case takes a form analogous to Eq. (11), with the difference that the HF exchange $\hat{K}$ will be substituted with the appropriate exchange-correlation term

$$\hat{F}_{\mathrm{DFT}}=\hat{T}+\hat{V}+\hat{J}+\hat{F}_{\mathrm{XC}}\ , \tag{19}$$

and the crystal HF equations will go over to the corresponding Kohn-Sham equations.[56] The self-consistent and gradient procedures for solids are again in complete analogy to the molecular case and the appropriate moduls of the G92/DFT program package[51] have been utilized, after extension for translational symmetry operations, for their solution. Several numerical and computational aspects of this procedure specific to infinite systems will be reported elsewhere.

The functionals used in our computations consist of separate exchange and correlation parts, respectively. For the exchange part, either the free-electron gas functional proposed by Slater (S),[58] or the gradient-corrected Becke functional (B) (Ref. 59) will be used. The correlation part will be either ignored (HFS and HFB theories, respectively) or it will be treated by the local-spin-density theory as parametrized by Vosko, Wilk, and Nusair (VWN) (Ref. 60) or by the gradient-corrected functional of Lee, Yang, and Parr (LYP) (Ref. 61) as transformed by Mielich *et al.*[62] Both correlation functionals can be combined with both exchange terms providing four different further schemes: S-VWN, S-LYP, B-VWN, and B-LYP, respectively.

III. MODELS AND RESULTS

A. HF-based perturbation theory

In order to obtain a first orientation for the quality of our theoretical models, we computed the binding energy and equilibrium internuclear distance of the hydrogen molecule and compared it with highly accurate theoretical results obtained previously.[63–65] The first column of Table I defines the atomic basis sets of systematically increasing size used in these studies. The exponents and coefficients of the starting 6s set of Gaussian-type orbitals (GTO's), contracted to four atomic orbitals according to the grouping 3/111, have been taken from Clementi's work,[66] while the exponents of the (uncontracted) polarization functions are from the correlation optimized sets of Dunning.[67] The smallest basis set contains four (contracted) atomic orbitals per hydrogen atom, while the largest one ($6s3p2d1f$) contains 31. The same basis sets have also been applied for the infinite systems.

A least-square fit to the HF and MP molecular total energies as functions of the number of the contracted GTO's, N_{CGTO}, with a polynomial of the type $p(N)=\sum_i A_i/N^i$, and extrapolation to the complete basis set limit ($N\equiv N_{\mathrm{CGTO}}\rightarrow\infty$) results in an estimated HF energy of $-1.133\,560$ hartree at the HF-optimized geometry, $-1.167\,123$ hartree for MP2, and $1.173\,288$ hartree for MP4, respectively. The estimated HF limit for H_2 is $-1.133\,668$ hartree,[63] close both to our ($6s3p2d1f$) basis set result of $-1.133\,473$ hartree and to the extrapolated value. The most accurate correlated [configuration interaction (CI)] energy reported for H_2 by Liu[64] using a ($5s3p3d2f$) set of Slater functions is $-1.174\,142$ hartree, while Kolos and Wolniewicz calculated an "exact" energy of $-1.174\,475$ hartree (Ref. 65) providing a correlation energy of $-0.020\,404$ hartree per H atom. Our MBPT wave functions result in $-0.016\,327$, $-0.018\,987$, and $-0.019\,714$ hartree per H atom at second, third, and fourth orders, respectively using the ($6s3p2d1f$) basis set (E). These methods thus recover 80, 93, and 96.6% of the full correlation energy. On the other hand, the importance of polarization functions is reflected in the fact that the ($6s$) basis set (A) provides only $-0.012\,619$ hartree (62%) in fourth order. The PT binding energies systematically converge to the exact value of $-0.174\,475$ hartree, the MP4 value of $\Delta E=-0.173\,019$ hartree containing only 0.8% error. At the same time, with $R=0.7405$ Å, the equilibrium bond distance of the H_2 molecule, 0.7408 Å,[68] also will be reasonably reproduced.

For the infinite equidistant (metallic) H-atom chain, the equilibrium lattice parameter systematically decreases at the HF level with the increasing size of the atomic basis set, from 0.9706 (set A) to 0.9620 Å (set E). Electron correlation, on the other hand, expands the lattice from 0.9620 Å at HF to 0.9698 Å at MP2, and to 0.9746 Å at the MP4 level of theory, respectively. The interatomic distance of the infinite chain is significantly larger at all theoretical levels (by 0.24–0.26 Å) than that of the hydrogen molecule. Figure 1 demonstrates the basis set dependence of the cohesion energy per H atom in the infinite equidistant chain as function of N_{CGTO}, using different theoretical approaches. Polarization functions with higher angular momenta seem to be especially important for the MP2 and MP4 energy contributions,

TABLE I. Equilibrium distance (R) and total energy of the hydrogen molecule computed at HF and various correlated levels using different atomic basis sets (energies in hartree, distances in Å).

Basis set[a]		E(HF)[b]	E(MP2)[c]	E(MP3)[d]	E(MP4)[d]	R(HF)	R(MP2)	R(MP4)
A:	$6s$	−1.128 386	−1.146 626	−1.151 892	−1.153 623	0.7323	0.7379	0.7456
B:	$6s1p$	−1.132 742	−1.160 758	−1.166 784	−1.168 342	0.7356	0.7389	0.7430
C:	$6s2p$	−1.133 331	−1.163 348	−1.169 337	−1.170 888	0.7339	0.7359	0.7405
D:	$6s2p1d$	−1.133 393	−1.165 205	−1.170 822	−1.172 313	0.7339	0.7365	0.7410
E	$6s3p2d1f$	−1.133 473	−1.166 127	−1.171 445	−1.172 899	0.7337	0.7359	0.7405

[a] The 6s basis set of Ref. 66 has been contracted in the form (6s/3111), while the polarization functions taken from Ref. 67 have been used without contraction.

[b] Obtained at the HF-optimized geometry.

[c] Obtained at the MP2-optimized geometry.

[d] Obtained at the MP4-optimized geometry.

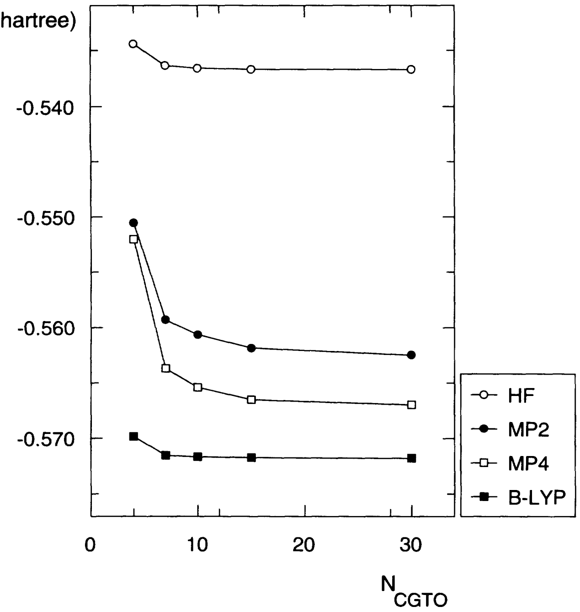

FIG. 1. Dependence of the cohesion energy per atom on the number of contracted Gaussian atomic basis functions (CGTO's) in the infinite equidistant chain of H atoms computed with different methods.

while the HF energies are practically convergent at the $(6s1p)$ basis set level. The $(6s2p1d)$ basis set, however, seems to be a very reasonable compromise for all methods. The single-particle energies are relatively independent of basis set effects, as shown by the nearly constant value of the Fermi level around -0.13412 hartree (basis set E).

Extrapolation of the HF and PT energies for an infinite basis set provides $-0.536\,746$ hartree as an estimate for the HF limit of the equidistant H-atom chain, and $-0.026\,819$ and $-0.030\,822$ hartree for E_{corr} at the MP2 and MP4 levels, respectively. Two remarks are in order concerning these quantities. First, as also observed in earlier studies,[16] the infinite equidistant H chain is not stable (at any level of theory) against dissociation into H_2 molecules since the binding energy per H atom in H_2 is always larger than in H_∞. However, electron correlation does somewhat stabilize H_∞ against H_2 by about -10 millihartree (mhartree) per electron, though it cannot compensate for the destabilization energy of $+30$ mhartree observed at the HF level. Second, intercellular (delocalized) interactions play an important role in E_{corr} and increase its value by about 40–50 % in each order of PT for H_∞ as compared to H_2. In addition, in fourth-order PT diagrams appear for H_∞ that do not play a role in H_2. For example, triple excitations contribute about -2.5 mhartree per electron to E_4 in the case of basis set (E).

For the quantum-mechanical calculation of the mechanical properties of solids, it is of primary importance to develop computational schemes that will be able to describe potential surfaces corresponding to nuclear configurations substantially different from those around equilibrium. It is well known, on the other hand, that the proper inclusion of electron correlation is especially important in such situations. To test the methods proposed in this paper for such problems, we first computed the lattice energy of a uniformly expanded equidistant H_∞ chain as function of the interatomic distance R using the RHF, MP2, and MP4 procedures with the $(6s3p2d1f)$ basis set (Fig. 2). The HF potential-energy surface shows the expected incorrect dissociation behavior due to its single-determinant closed-shell wave function. It is interesting, however, that the MP2 potential is still rather far from the physically correct one (achieved by the MP4 method). As shown by Fig. 2, this problem can be traced back to the fact that though the MP2 method covers about 80–85 % of the correlation for a given basis set in the neighborhood of the equilibrium configuration, R_0, its proportion drops rapidly to 45–50 % by moving away from R_0.

Another, though related, problem is the proper energetic description of lattice dimerization effects. Such mechanisms not only play an important role in the conductive properties of several polymer crystals by fundamentally changing their electronic states (e.g., through metal-to-semiconductor transitions), but are also intimately connected with the properties of several important phonon modi. To compare the performance of our methods again, we calculated the energetic changes due to the introduction of a bond alternation into the previously equidistant H_∞ chain. As shown in Fig. 3, the bond-alternation parameter $d = R_1 - R_2$ will characterize different configurations of this $(H_2)_\infty$ chain. In these model calculations, the bond-alternating structures were symmetrically generated from the corresponding optimized equidistant chains by taking $R_1 = R_0 + d/2$ and $R_2 = R_0 - d/2$. A remarkable feature of the dimerization

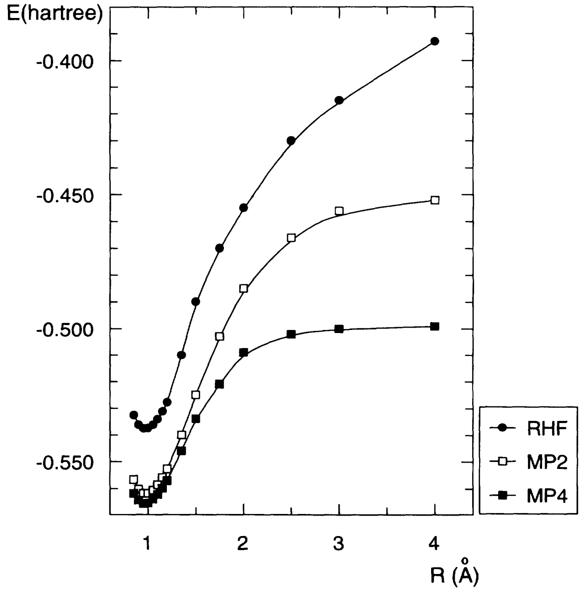

FIG. 2. Dissociation properties of the infinite equidistant chain of H atoms as described by restricted HF (RHF)-based perturbation theories. The energy per H atom has been computed using the $6s3p2d1f$ atomic basis set.

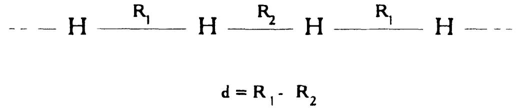

FIG. 3. Definition of the dimerization parameter d in the bond-alternating infinite H-atom chain.

process is the very different role played by the various PT terms in going from the $E_{\mathrm{HF}}(d)$ curve to the $E_{\mathrm{MP4}}(d)$ one as depicted in Fig. 4. In summary, we can see that correlation effects somewhat reduce the dimerization amplitude and substantially diminish (especially through the $\mathcal{E}^{(2)}$ term) the dimerization energy (measured from the energy per H atom in the equidistant chain).

B. UHF-based perturbation theory

The influence of the relaxation of the spin symmetry has been investigated by assigning the α- and β-spin electrons to different Bloch orbitals, first in the framework of the unrestricted Hartree-Fock (UHF) procedure. The 6*s* atomic basis set has been used in these computations, but the overall conclusions apply to the polarized basis sets as well. It is interesting to note here that, contrary to the H_2 molecule, the H_∞ chain always proves to be triplet instable[71] (also for nuclear configurations close to equilibrium). The UHF wave function introduces in all cases a substantial difference between α- and β-spin densities (0.38–0.40 electron per site). Parallel to building up this spin density, the lattice expands by 0.02–0.03 Å and the energy decreases ($E_{\mathrm{UHF}} - E_{\mathrm{HF}} \approx -5$ mhartree). Φ_{UHF}, however, turns out to be not as advantageous as Φ_{HF} for the use of zeroth-order many-electron wave functions in PT. Despite the better start by -5 mhartree, the UHF-based PT energies always lie higher than the corresponding MP2 and MP4 ones (by 3.144 and 0.748 mhartree for UMP2 and UMP4, respectively). Formally, this can be traced back to the artificially large energy gap introduced by the UHF method into the single-particle energy spectrum. Though the position of the Fermi level is unchanged for the HF-to-UHF transition, a gap of about 0.3 hartree appears for UHF that substantially increases the energy denominators in PT. The lattice constant increases from 0.9776 (MP2) to 1.0144 (UMP2) and from 0.9855 (MP4) to 1.0188 Å (UMP4).

It may also be of interest to observe that different terms of PT will be influenced in a very different manner by the UHF-type choice of the zeroth-order state. While $\mathcal{E}^{(2)}$ will be reduced from -16.469 (HF) to -7.880 mhartree (UHF), $\mathcal{E}^{(3)}$ increases from -1.837 to -2.435, $\mathcal{E}_S^{(4)}$ remains nearly unchanged, $\mathcal{E}_{\mathrm{DQ}}^{(4)}$ mutates from $+0.364$ to -0.993, and $\mathcal{E}_T^{(4)}$ from -1.469 to $+0.051$ mhartree, respectively. Due to associating different Bloch orbitals with different spins in the zeroth-order UHF many-electron wave function, all versions of the spin-unrestricted theory (from UHF to UMP4) display an excellent dissociation behavior, as shown by Fig. 5. This property predestinates them to provide a sound theoretical basis for studies of elastic properties of solids.[69,70]

C. Density-functional theory

As mentioned in Sec. II, we applied six different functional forms of the DFT theory to compare their performance with the HF, MP2, and MP4 methods, respectively. As for these latter procedures, we will first turn to the H_2 molecule to determine the accuracy of the DFT methods in predicting equilibrium bond distances (R)

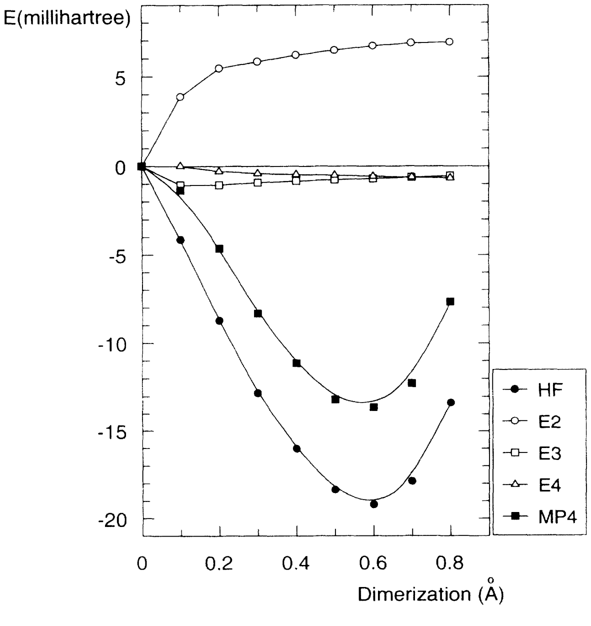

FIG. 4. The energy contribution per H atom of different terms in the fourth order of MBPT as a function of the dimerization parameter in the bond-alternating infinite chain shown in Fig. 3 (basis set: 6*s*1*p*).

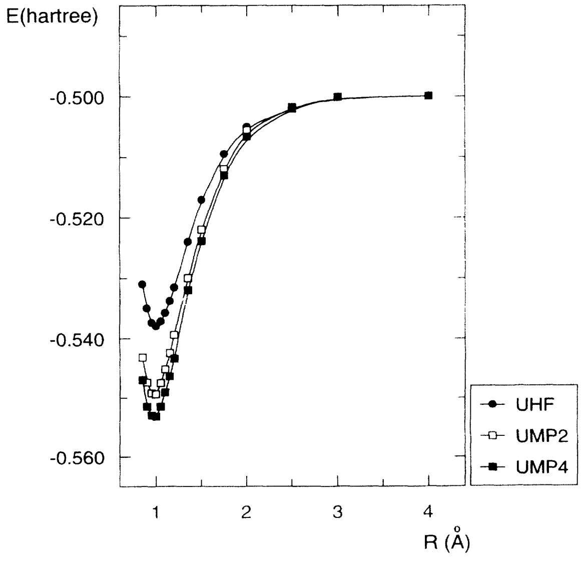

FIG. 5. Dissociation properties of the infinite equidistant chain of H atoms as described by unrestricted HF (UHF)-based perturbation theories. The energy per H atom has been computed using the 6*s*1*p* atomic basis set.

TABLE II. Energy of the H atom, equilibrium distance (R), total energy (E), and binding energy (ΔE) of the hydrogen molecule, respectively, computed at various theoretical levels using the $6s3p2d1f$ atomic basis set. The different density functionals are defined in the text (energies in hartree, distances in Å).

Method	E(H atom)	$R(H_2$ molecule)[a]	$E(H_2$ molecule)[b]	$\Delta E(H_2$ molecule)
HF	−0.499 940	0.7337	−1.133 473	−0.133 593
MP2	−0.499 940	0.7359	−1.166 127	−0.166 247
MP4	−0.499 940	0.7405	−1.172 899	−0.173 019
HFS	−0.456 958	0.7819	−1.044 504	−0.130 558
HFB	−0.497 802	0.7523	−1.132 029	−0.136 425
S-VWN	−0.496 322	0.7634	−1.173 130	−0.180 486
S-LYP	−0.456 958	0.7748	−1.082 169	−0.168 253
B-VWN	−0.537 674	0.7353	−1.262 370	−0.187 022
B-LYP	−0.497 802	0.7458	−1.170 117	−0.174 513

[a] Experiment: $R = 0.7408$ Å (Ref. 68).

[b] Exact value: $E = -1.174\,475$ hartree (Ref. 65).

and binding energies (ΔE). As expected, the HF*S* and HF*B* methods provide a good estimate of the HF binding energy while the correlated ones reasonably describe E_{corr} (Table II). The Vosko, Wilk, and Nusair (VWN) (Ref. 60) correlation functional seems somewhat to overestimate the binding energy as compared with the gradient-corrected functional of Lee, Yang, and Parr (LYP).[61] The most accurate binding energy will be obtained by the *B*-LYP method, with $\Delta E = -0.174\,513$ hartree, as compared with the MP4 ($-0.173\,019$ hartree) and exact ($-0.174\,475$ hartree) values, respectively. The Slater exchange tends to overestimate the bond distance (R), though this error will be reduced by the correlation potentials. On the other hand, both the *B*-VWN and *B*-LYP combinations provide very reasonable values for R.

In the case of the equidistant infinite chain, the expansion of the lattice by 0.24–0.26 Å (in going from H_2 to H_∞) as observed for the wave-function methods, will be exactly reproduced by all DFT procedures (Table III). If we take the MP4 value of R as reference for H_∞, we can see both the *B*-VWN and *B*-LYP methods provide very accurate lattice parameters, in agreement with the corresponding observation above for H_2. Further comparing the performance of the PT and DFT methods, we can observe that the *B*-LYP functional gives an excellent estimate for the lattice energy: $-0.571\,532$ hartree vs $-0.563\,712$ hartree (MP4 value for basis set *B*). The HF-Fermi energy will be shifted by about -0.03 to -0.06 hartree for different DFT procedures. These values quite reasonably compare with the correlation-induced quasiparticle band shifts to be discussed below.

We have investigated the basis set dependence of the structural and energetic predictions of DFT in more detail for the *B*-LYP functional. It turned out that the DFT properties exhibit the same behavior as the HF ones, and converge in this respect much faster than the PT methods. A similar conclusion (but in a negative sense) can be drawn concerning the dissociation properties of DFT functionals. Figure 6 compares the *B*-LYP and *B*-VWN methods with the HF- and MP4-based procedures. Both DFT methods behave HF-like in the absence of explicitly introduced spin polarization.

Figures 7 and 8 present our results obtained by studying the energetics of lattice dimerization (Fig. 3) within DFT schemes using the ($6s1p$) atomic basis set. It appears that for DFT the correlation contributions depend less strongly on the dimerization amplitude than their PT counterpart. In the case of functional combinations with Slater exchange (Fig. 7), the correlation terms prove to be unimportant and lead to an optimized value of $d = 0.40$–0.45 Å for all three functionals, shorter than the MP4 prediction of $d = 0.59$ Å. The functionals using Becke exchange (Fig. 8) show more diversity and a stronger influence of correlation effects. Their minima lie in the range of $d = 0.47$–0.55 Å. Their prediction of the dimeric stabilization energy (-7 to -9 mhartree) is somewhat smaller than the MP4 value of -12.5 mhartree but definitely better than that of the Slater exchange group (-3 to -4 mhartree).

At last, we have followed the development of the single-particle energy gap E_g as a function of dimerization using the *B*-LYP potential and the ($6s1p$) basis set. The HF values of E_g in Fig. 9 have been corrected for correlation effects using the electron-polaron method[37] at the MP2 level. Besides a Frank-Condon-type band narrowing due to polaron formation, this method predicts a

TABLE III. Energy per hydrogen atom (E), optimized lattice constant (R), and Fermi energy obtained for the infinite equidistant hydrogen atom chain using PT and DFT methods, respectively, and the $6s1p$ atomic basis set (energies in hartree, distances in Å).

Method	E	R	E(Fermi)
HF	−0.536 357	0.9634	−0.126 71
MP2	−0.559 326	0.9711	
MP4	−0.563 712	0.9753	
HFS	−0.514 418	1.0175	−0.119 22
HFB	−0.549 528	1.0058	−0.131 74
S-VWN	−0.579 687	0.9902	−0.174 11
S-LYP	−0.536 276	0.9984	−0.141 35
B-VWN	−0.615 374	0.9796	−0.187 06
B-LYP	−0.571 532	0.9868	−0.153 88

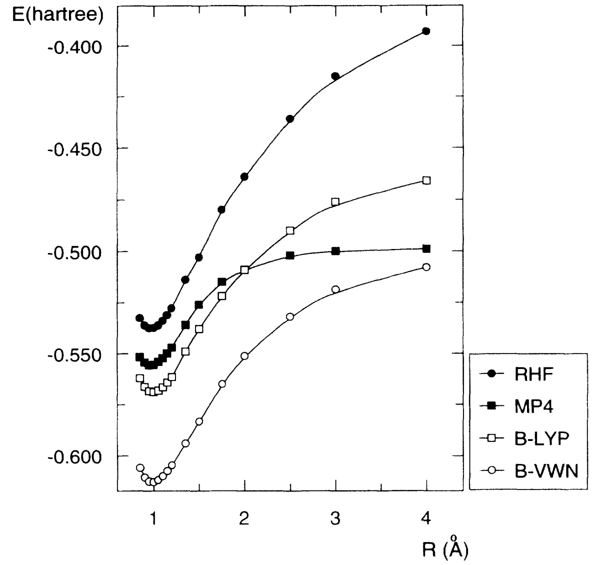

FIG. 6. Comparison of the dissociation properties of the infinite equidistant chain of H atoms obtained at the RHF and MP4 levels, respectively, and using density-functional theory with the B-LYP and B-VWN potentials, respectively. The energy per H atom has been computed using the $6s\,1p$ atomic basis set.

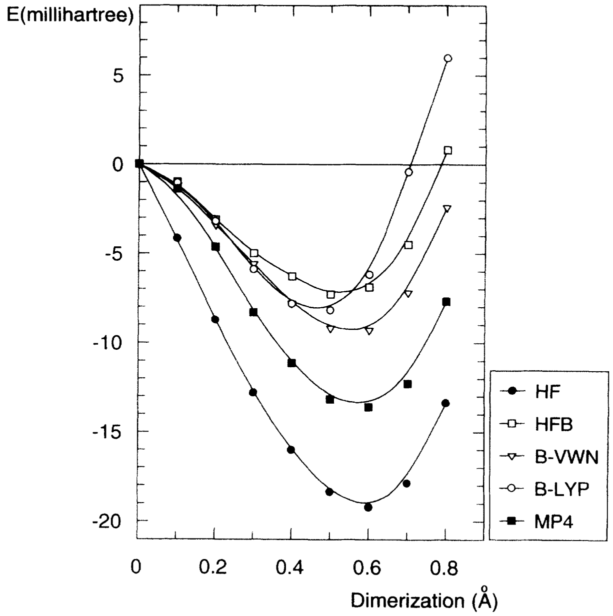

FIG. 8. The energy per hydrogen atom obtained at the HF and MP4 levels in the bond-alternating infinite chain compared with the results of density-functional theories using the Becke exchange potential (atomic basis set: $6s\,1p$).

correlation-induced upward shift of the valence band and a downward shift of the conduction band leading to an effective reduction of the (obviously too large) HF gap. Since this method has provided quite reasonable E_g values for a number of polymer crystals where experimental values could be cited for comparison,[42–46] we may assume that the MP2 curve in Fig. 9 gives a good orientation for the $E_g(d)$ function. A similar reduction of the HF gap for H_∞ by about 0.03 hartree due to correlation has also been observed by Liegener[28] at the MP3 level of theory. We have to conclude, therefore, that the single-particle gaps provided by the DFT method are much too low (approximately by a factor 2). This is not an unusual observation, and it may serve as a motivation to further correct the E_g results of DFT by introducing appropriate schemes.[72]

IV. DISCUSSION AND CONCLUSIONS

The purpose of this study was the critical comparison of perturbation theoretical and density-functional methods in describing the role of electron correlation in various physical properties of solids both for equilibrium nuclear configurations (cohesive properties, lattice dimer-

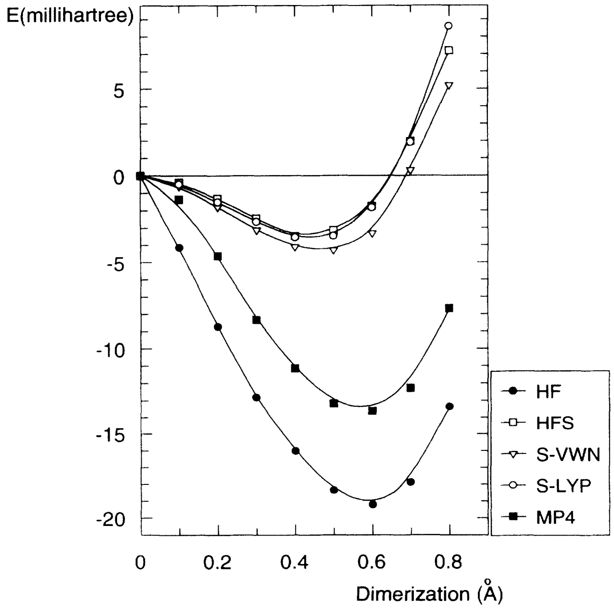

FIG. 7. The energy per hydrogen atom obtained at the HF and MP4 levels in the bond-alternating infinite chain compared with the results of density-functional theories using the Slater exchange potential (atomic basis set: $6s\,1p$).

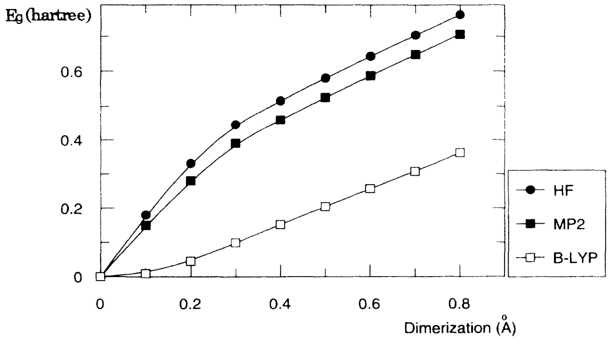

FIG. 9. Dependence of the single-particle energy-band gap on the dimerization parameter at the HF, MP2, and DFT/B-LYP levels, respectively (atomic basis set: $6s\,1p$).

ization effects, etc.) and nonequilibrium ones (large amplitude vibrations, elongation, dissociation, etc.). Besides many-electron properties, we also calculated single-particle ones like Fermi energies, energy bandwidths, and forbidden band gaps. For model systems we chose the equidistant (metallic) and bond-alternating (semiconducting) infinite linear chains of H atoms. In addition to being the simplest solids, these models have the great advantage that their molecular counterpart, the H_2 molecule, is the theoretically best understood model, providing an excellent opportunity to check the accuracy of any theoretical approach to be applied to the infinite system.

Also, to gain insight into the atomic basis set dependence of these methods, we have performed most of the calculations for five basis sets starting with a quadruple-ζ basis contracted from six s-type Gaussians, and systematically extended it with polarization functions up to f-type orbitals. This procedure allowed for the extrapolation of some quantities to the "infinite basis set limit." We found that our best basis set, the $(6s3p2d1f)$, reproduces the HF energy limit of H_2 with an accuracy of 99.98% and it provides 80, 93, and 96.6% of the full correlation at the MP2, MP3, and MP4 levels, respectively. The MP4 bond distance has an error of only 0.0003 Å and the molecular binding energy is accurate to 99.17% (Table I). From the DFT methods, Becke's exchange potential[59] (HFB procedure) excellently approaches the HF binding energy (ΔE) of H_2 (within 2%) and, combined with the gradient-corrected correlation potential of Lee, Yang, and Parr,[61] it nearly exactly reproduces the correlated limit of ΔE (Table III). As expected, the PT methods depend sensitively on the size of the basis set, while both the HF and DFT procedures practically converge at the $(6s1p)$ level.

The interatomic distance in the equidistant infinite chain (H_∞) is larger by about 0.25 Å than in H_2, and, consequently, the binding energy will be smaller in H_∞ than in the isolated molecule. Our estimated HF limit for the cohesion energy of H_∞ is $-0.036\,746$ hartree/atom, somewhat larger than the value of -0.0361 proposed by Karpfen,[19] who terminated the basis sets at the $(6s1p)$ level. On the other hand, ΔE_{HF} of H_2 is $-0.066\,834$ hartree/atom. As expected, the electron correlation will reduce the difference in the cohesion between H_∞ and H_2. The correlated binding energy of H_∞ is $-0.067\,524$ hartree per atom at the MP4/$6s3p2d1f$ level (Table II), as compared with $-0.086\,450$ hartree per atom in H_2 (Table I). Similar to the case of H_2, for polarized basis sets the major part of E_{corr} (about 85%) originates from $\mathcal{E}^{(2)}$; $\mathcal{E}^{(3)}$ and $\mathcal{E}^{(4)}$ contribute about 10% and 5%, respectively. A similar observation was made by Liegener[28] for the second- and third-order terms, respectively. For the DFT methods, the B-LYP functional combination gives the best estimate of the cohesion energy in H_∞ ($-0.073\,730$ hartree/atom) and also its equilibrium distance of 0.9868 Å reasonably reproduces the MP4 value of 0.9746 Å.

In order to explore the capabilities of the above methods for atomic configurations differing from equilibrium structures, the lattice of H_∞ was uniformly expanded. Not only the HF and MP2 (Fig. 2), but also the DFT methods fail to reproduce the correct behavior of the cohesion at larger internuclear distances (Fig. 6). In fact, from the methods operating with closed-shell configurations or with PT based on such configurations, only the MP4 procedure could properly predict the dissociation of H_∞ (Fig. 2). The situation is completely different, however, if an open-shell (spin-unrestricted) many-electron wave function is used as the starting point for PT. As demonstrated by Fig. 5, all versions of this theory (UHF, UMP2, and UMP4) lead to correct dissociation. It turns out, on the other hand, that the UHF method does not provide a good basis for the computation of E_{corr} around the equilibrium, where the UMP series converge significantly slower than their MP counterparts.

Since different structural phase transitions like bond dimerization (Peierls instability) play an important role in several interesting polymer crystals, we investigated the energetics of such processes again using parallel PT and DFT. For the symmetrical distortion of the H_∞ lattice about equilibrium (R_0), the HF method predicts an optimal dimerization of $d_{\mathrm{HF}}=0.59$ Å (Figs. 3 and 4) and a parallel energy gain of $E_{\mathrm{HF}}^{(d)}=-18.9$ mhartree. Correlation effects somewhat reduce both quantities leading to $d_{\mathrm{MP4}}=0.56$ Å and $E_{\mathrm{MP4}}^{(d)}=-12.5$ mhartree (Fig. 4). The combinations of the VWN or LYP correlation potentials with the local exchange (S) quantitatively underestimate this effect both from the energetic and structural points of view (Fig. 7). After correction of E_X with gradient terms, the results obtained with the DFT methods will be improved substantially. The best agreement with the MP4 ones can be observed for the B-VWN potential: $E_{B\text{-VWN}}^{(d)}=-9.4$ mhartree and $d_{B\text{-VWN}}=0.55$ Å. A similar bond alternation of $d=0.6$ Å has been predicted for H_∞ by Liegener[28] using a minimal basis set at the MP3 level and by Ye, Förner, and Ladik[33] using coupled cluster doubles (CCD) theory. As can be seen from Fig. 4, E_{corr} steadily decreases with increasing bond alternation a feature also reasonably reproduced by the DFT methods (Fig. 8) but not by the CCD theory. We attribute this difference partly to the limited lattice sums (third-neighbor cutoff) in Ref. 33 leading to the reported numerical instabilities for larger basis sets due to linear dependences, and partly to the transformation to Wannier functions in the case of the equidistant (metallic) chain.[33] This point emphasizes again the importance of using the Bloch basis for PT calculations in metallic systems.[24]

Besides energetically stabilizing the lattice, the Peierls distortion also introduces a gap into the single-particle energy spectrum. Our preliminary calculations performed only with B-LYP potentials reveal that this gap seems to be underestimated when compared with the corresponding values obtained at the MP2 level. Similar comparative investigations (using PT and DFT methods) are also in progress in our laboratory for other polymer crystals, to gain more insight into the capabilities and limitations of these theoretical procedures. Our special interest will be devoted to systems in which ample experimental results will further facilitate such comparisons.

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