On the ground state of solids with strong electron correlations

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Abstract

We formulate the calculation of the ground-state wavefunction and energy of a system of strongly correlated electrons in terms of scattering matrices. A hierarchy of approximations is introduced which results in an incremental expansion of the energy. The present approach generalizes previous work designed for weakly correlated electronic systems.
I. INTRODUCTION

A microscopic wavefunction-based description of electron correlations in the ground state of extended systems, i.e., large molecules or solids remains a challenging problem. This holds particularly true when the correlations are strong. Much progress has been achieved though over the last twenty years. For example, it has become clear that local operators have to be applied for describing the correlation hole of the electrons [1-6]. Otherwise calculations with controlled approximations for extended systems become nonfeasible. When starting from a self-consistent field (SCF) wavefunction for the ground state denoted by $|\Phi_0>$ the wave operator $\tilde{\Omega}$, which transforms it into the true ground-state wavefunction $|\Psi_0>$ must be constructed from local operators $A_\nu$. They describe one-, two- or generally multiparticle excitations out of $|\Phi_0>$. The fact that the $A_\nu$ are local operators implies that the creation and annihilation operators appearing in $A_\nu$ refer to local orbitals instead of canonical orbitals or Bloch states.

The first ground-state calculations based on the use of local operators were done for diamond [7]. However, it was not until the method of increments was pointed out [5,8], that a large number of solids were successfully treated by quantum-chemical configuration-interaction (CI) techniques (see, e.g., [8-10]). Although most of the calculations were done with respect to the ground-state wavefunction it was shown that the same ideas can be also applied to the calculation of excited states, i.e., energy bands of a solid [11].

The calculations described above were done for systems in which electron correlations are not too strong, i.e., for which the SCF configuration is a good starting-point. If the electronic correlations are strong one should not start from the independent-electron approximation when attempting to calculate
the true ground-state wavefunction. It has been suggested that the method of
increments can be also applied to strongly correlated systems by performing
multi-configuration SCF (MCSCF) or complete-active-space SCF (CASSCF)
calculations for localized orbital groups [12]. But the theoretical formulation
of such an approximation scheme as well as the form of the ground-state wave
function have remained unclear.

The aim of the present communication is to provide a basis for the incre-
mental method when the correlations are strong. For that purpose we have to
modify a derivation of an incremental scheme given in Ref. [13]. We want to
show how one can construct a cumulant wave operator for strongly correlated
electron systems. This operator defines the ground-state of the system.

The paper is organized as follows. In the next section a frame is provided
for the computation of the ground state of a strongly correlated extended
electron system by means of quantum-chemical methods. Section III demon-
strates explicitly how the calculations have to be done in practice. Section IV
contains a summary and the conclusions.

II. FORMALISM

Starting point is the Hamiltonian $H$ of the electronic system

$$H = \sum_{ij\sigma} t_{ij} a_{i\sigma}^+ a_{j\sigma} + \frac{1}{2} \sum_{ijkl\sigma\sigma'} V_{ijkl} a_{i\sigma}^+ a_{k\sigma'}^+ a_{l\sigma'} a_{j\sigma}. \quad (1)$$

It refers to a given basis set $f_i(r)$ for which usually Gauss-type (GTO) or
Slater-type orbitals are chosen. The matrix elements $t_{ij}$ and $V_{ijkl}$ refer to the
one-electron (including kinetic energy) and two-electron interaction energy,
respectively. We split $H$ into a self-consistent field part $H_{SCF}$ and a residual
interaction part $H_{res}$. The latter is given, for the closed-shell case, e.g., by
\[ H_{\text{res}} = \sum_{ijkl} \left[ \frac{1}{2} \sum_{\sigma\sigma'} V_{ijkl} a_{k\sigma}^+ a_{l\sigma'}^+ - \sum_{\sigma} \left( V_{i\ell kj} - \frac{1}{2} V_{i\ell kj} \right) P_{k\ell} a_{i\sigma}^+ a_{j\sigma} \right. 
+ \left. \frac{1}{2} \left( V_{ijkl} - \frac{1}{2} V_{i\ell kj} \right) P_{ij} P_{k\ell} \right]. \]  

(2)

The one-particle density matrix \( P_{ij} \) is defined by

\[ P_{ij} = \sum_{\sigma} < a_{i\sigma}^+ a_{j\sigma} > \]  

(3)

and \(< ... > = < \Phi_{\text{SCF}} | ... | \Phi_{\text{SCF}} > \) with \( \Phi_{\text{SCF}} \) denoting the ground state of \( H_{\text{SCF}} \). It is noticed that \( H_{\text{res}} \) consists of a constant term plus one- and two-particle excitations. We subdivide \( H_{\text{res}} \) further into

\[ H_{\text{res}} = \sum_{I} H_{I} + \sum_{I,J} H_{IJ}. \]  

(4)

Here \( H_{I} \) denotes that part of \( H_{\text{res}} \) where excitations are restricted to a group of localized orbitals belonging to center \( I \) (e.g., an atom or a bond), while \( H_{IJ} \) contains the part in which the centers \( I \) and \( J \) are involved in the process of creating holes. For example, van der Waals type interactions between atoms (or bonds) \( I \) and \( J \) belong to \( H_{IJ} \) since they involve a one-particle excitation on each of the atoms (bonds) \( I \) and \( J \). This division of \( H_{\text{res}} \) differs from the one in Ref. [13] where \( H_{\text{res}} \) was decomposed into contributions corresponding to different pairs of holes generated out of the self-consistent ground state \( | \Phi_{\text{SCF}} > \).

We characterize the ground state of \( H \) by the cumulant wave operator \( | \Omega > \) [14, 6]. The conventional wave operator \( \tilde{\Omega} \) is defined as the one which transforms \( | \Phi_{\text{SCF}} > \) into the exact ground state \( | \Psi_{0} > \), i.e., \( | \Psi_{0} > = \tilde{\Omega} | \Phi_{\text{SCF}} > \). The cumulant wave operator \( | \Omega > \) differs from \( \tilde{\Omega} \) in that it is defined in a space with a different metric than that, e.g., of the conventional Hilbert or operator space. Here the metric is defined by the following bilinear form of two general operators \( A \) and \( B \).

\[ (A | B) = < \Phi_{\text{SCF}} | A^+ B | \Phi_{\text{SCF}} >^c. \]  

(5)
The upper script $c$ implies taking the cumulant of that expression [14,15,6]. The usefulness of cumulants in quantum mechanics was stressed by Kubo [15] who generalized earlier work of Ursell and Mayer in classical statistical mechanics [16]. Cumulants have the advantage that they correspond to linked clusters. Therefore the problem of size consistency (or extensivity) does not exist when quantities are expressed in terms of them. For further information we refer to, e.g., Ref.[6]. In accordance with the above the ground-state energy is given by

$$E_0 = \langle H | \Omega \rangle.$$  \hfill (6)

The cumulant wave operator is of the form [6]

$$| \Omega \rangle = \lim_{z \to 0} \left| 1 + \frac{1}{z - H} H_{res} \right).$$  \hfill (7)

In accordance with Ref. [13] we define a scattering operator

$$| S \rangle = | \Omega - 1 \rangle = \lim_{z \to 0} \sum_{n=1}^{\infty} \left( \frac{1}{z - H_{SCF}} H_{res} \right)^n.$$  \hfill (8)

In proceeding we use an argument developed in [13] which can be considered as a generalization of Faddeev’s equation. Faddeev derived an equation [17] which expresses the scattering operator of a three-particle system in terms of the scattering matrices for the different two-particle channels. For the latter often analytic solutions can be found. More generally, we aim at expressing the scattering operator of an $\tilde{N}$ electron system in terms of scattering matrices of simpler subsystems. With this goal in mind we introduce the operators

$$A_{II} = \lim_{z \to 0} \frac{1}{z - H_{SCF}} H_I, \quad A_{IJ} = \lim_{z \to 0} \frac{1}{z - H_{SCF}} H_{IJ}.$$  \hfill (9)

With their help we rewrite

$$| S \rangle = \sum_{n=1}^{\infty} \left( \sum_{I,J} A_{IJ} \right)^n.$$  \hfill (10)
where \( N \) is the number of centers, i.e., atoms (bonds) in the system. We introduce Greek letters to denote pair labels \( IJ \) so that \( \sum_{IJ} | A_{IJ} > = \sum_{\alpha} | A_{\alpha} > \) and decompose \( | S \rangle \) into terms with one Greek index and a remaining part. Therefore we write

\[
S = \sum_\alpha \left( \sum_{n=1}^{\infty} A^n_\alpha \right) + \sum_{\alpha \neq \beta} T_{\alpha\beta}
\]

\[
= \sum_\alpha S_\alpha + \sum_{\alpha \neq \beta} T_{\alpha\beta}.
\]

The \( T_{\alpha\beta} \) are defined as follows: When \( 10 \) is decomposed into different terms we include in \( T_{\alpha\beta} \) all those which begin with \( A_\alpha \) from the left followed by \( A_\beta \) as the first factor different from \( A_\alpha \). For example, terms of the form \( A_\alpha A_\beta \ldots, A_\alpha A_\alpha A_\beta \ldots, A_\alpha A_\beta A_\beta \ldots \) are all included in \( T_{\alpha\beta} \). With this definition we can write

\[
T_{\alpha\beta} = (A_\alpha A_\beta + A_\alpha A_\beta A_\alpha + \ldots) \cdot \left(1 + \sum_{\gamma \neq \alpha,\beta} S_\gamma + \sum_{\gamma \neq \alpha,\beta;\delta} T_{\gamma\delta}\right).
\]

When adding \( T_{\alpha\beta} + T_{\beta\alpha} \) one notices that the first bracket is nothing else but the scattering operator \( S_{\alpha\beta} \) of a Hamiltonian \( H_{SCF} + H_\alpha + H_\beta \), except that the contributions \( S_\alpha + S_\beta \) are missing. Therefore we can write

\[
T_{\alpha\beta} + T_{\beta\alpha} = (S_{\alpha\beta} - S_\alpha - S_\beta) \left(1 + \sum_{\gamma \neq \alpha,\beta} S_\gamma + \sum_{\gamma \neq \alpha,\beta;\delta} T_{\gamma\delta}\right).
\]

or

\[
S = \sum_\alpha S_\alpha + \sum_{<\alpha\beta>} (S_{\alpha\beta} - S_\alpha - S_\beta) \left(1 + \sum_{\gamma \neq \alpha,\beta} S_\gamma + \sum_{\gamma \neq \alpha,\beta;\delta} T_{\gamma\delta}\right).
\]

Here \( <\alpha\beta> \) denotes different pairs.

One expects that the matrix elements of \( H_I \) are generally much larger than those of \( H_{IJ} \). Therefore it seems advantageous to introduce approximations
to $|S\rangle$ by resumming the right hand side of the last equation according to different numbers of sites involved. To lowest order $|S\rangle$ is therefore given by

$$|S\rangle = \sum_I S_I,$$

(14)

where $S_I = S_\alpha$ with $\alpha = II$ is the scattering operator of Hamiltonian $H_{SCF} + H_I$.

In this single-site approximation

$$E_0 = E_{SCF} + (H | S)$$

$$= E_{SCF} + \sum_I \epsilon_I$$

with $\epsilon_I = (H | S_I)$. In next order we include the terms $S_\alpha$ with $\alpha = IJ$ and $T_{\alpha\beta}$ with $\alpha$ and $\beta$ being $II, JJ, IJ$ and $JI$. In this two-sites approximation the second bracket in (12) is replaced by unity. By adding up the different contributions we find

$$|S\rangle = \sum_I |S_I\rangle + \sum_{<IJ>} |S_{IJ} - S_I - S_J\rangle$$

where $S_{IJ}$ is the scattering operator belonging to $H_{SCF} + H_I + H_J + H_{IJ} + H_{JI}$.

Furthermore,

$$E_0 = E_{SCF} + \sum_I \epsilon_I + \sum_{<IJ>} \epsilon_{IJ}$$

(16)

with $\epsilon_{IJ} = (H | S_{IJ}) - \epsilon_I - \epsilon_J$. This procedure can be continued. By including also three-sites terms we find

$$|S\rangle = \sum_I |S_I\rangle + \sum_{<IJ>} |\delta S_{IJ}\rangle + \sum_{<IK>} |\delta S_{IK}\rangle + \sum_{<IJK>} |\delta S_{IJK}\rangle + \ldots$$

(17)

with $|\delta S_{IJ}\rangle = |S_{IJ}\rangle - |S_I\rangle - |S_J\rangle$ as before and

$$|\delta S_{IJK}\rangle = |S_{IJK}\rangle - |\delta S_{IJ}\rangle - |\delta S_{JK}\rangle - |\delta S_{IK}\rangle - |S_I\rangle - |S_J\rangle - |S_K\rangle.$$

(18)
Here $| S_{IJK} \rangle$ is the scattering operator of a Hamiltonian $H = H_{SCF} + H_I + H_J + H_K + H_{IJ} + H_{IK} + H_{JK} + H_{JI} + H_{KI} + H_{KJ}$. This approximation scheme can be continued until finally the exact scattering operator $| S \rangle$ is obtained. The corresponding energy expression (15) is then

$$E_0 = E_{SCF} + \sum_I \epsilon_I + \sum_{<IJ>} \epsilon_{IJ} + \sum_{<IJK>} \epsilon_{IJK} + ...$$

with

$$\epsilon_{IJK} = (H | S_{IJK} \rangle - \epsilon_I - \epsilon_J - \epsilon_K - \epsilon_I - \epsilon_J - \epsilon_K$$

etc.

The advantage of the above formalism is that we have reduced the ground-state calculations for extended systems like solids to the computation of single-center, two-center etc. scattering matrices. These matrices can be determined by means of quantum-chemical methods whereby all the other electrons in $| \Phi_{SCF} \rangle$ are kept frozen. There is no difficulty in calculating the scattering matrices also when the electrons are strongly correlated. For example, multiconfiguration SCF (MCSCF) calculations or complete-active-space SCF (CASSCF) calculations, followed by a multireference CI (MRCI) treatment, serve that purpose. Strong correlations can therefore be treated with a high degree of accuracy in ground-state calculations for solids.

III. APPLICATIONS

In the following we want to outline in some more detail how ground-state calculations for strongly correlated electron systems have to be performed. We limit ourselves to insulators or semiconductors, i.e., systems with a gap in the excitation spectrum. Starting point is the Hamiltonian (1) acting in a space
spanned by a properly chosen basis set of GTO’s. After a SCF calculation has been performed, e.g., by using the program package CRYSTAL [18] or the code developed by Shukla et al. [19], one has to express the SCF orbitals in the form of orthogonal localized Wannier orbitals. This is achieved either by an a-posteriori localization procedure if CRYSTAL is used, or by using Shukla’s program which yields directly the occupied SCF orbitals in localized form. The corresponding creation and annihilation operators are denoted by $\tilde{c}_{\ell\sigma}^\dagger$, $\tilde{c}_{\ell\sigma}$. For the strongly correlated electrons in the system, e.g., the $d$ electrons of a transition metal atom or the $f$ electrons of a rare earth or actinide atom, we need to express in localized form not only the occupied, but also the unoccupied (virtual) $d$ or $f$ orbitals. Finding them poses no problem and we include them in the set of operators $\tilde{c}_{\ell\sigma}^\dagger$, $\tilde{c}_{\ell\sigma}$. In the next step the residual interactions $H_{res}$ are expressed in terms of the $\tilde{c}_{\ell\sigma}^\dagger$, $\tilde{c}_{\ell\sigma}$ operators. Except for the strongly correlated electrons we express only the annihilation operators in (2) in terms of the $\tilde{c}_{\ell\sigma}$. (The external orbitals have to be localized, but they need not being orthogonal to each other, cf. e.g. [20].) The strong correlations are treated by a CASSCF calculation. The choice of the active space depends on the scattering matrix we want to calculate. For the determination of the $S_I$ we choose the strongly correlated orbitals of that center (e.g., the localized $d$ or $f$ orbitals of an atom or the bonding and anti-bonding orbitals of a bond) for the active space. With all electrons kept frozen except those on center $I$, the CASSCF calculation with the active space involving orbitals on that center only accounts for the strong intra-atomic (or intra-bond) correlations. When $S_{IJ}$ is calculated we must include in the active space the localized $d(f)$ orbitals (or bonding/antibonding orbitals) on centers $I$ and $J$. The resulting ground state is denoted by $|\Psi_0\rangle$. After every CASSCF calculation, the remaining (weak) correlations may be accurately taken into account by means of calculations within some variant of the coupled electron pair approximation.
(e.g., MRCEPA or MRACPF with single and double excitations into the external space). In case that the two-center scattering matrices $S_{IJ}$ are not sufficient for an accurate determination of $|\Omega\rangle$ one can extend the calculations to three-center scattering matrices $S_{IJK}$.

Let us apply now the above considerations to simple molecular examples involving hydrocarbons. We address the question of how to properly treat such systems in the strong-correlation limit of dissociation into separate atoms; the ultimate goal of our investigation being a unified treatment of $C_\infty$ (diamond) for a wide range of C-C internuclear distances. Specifically, we performed calculations for CH$_4$, C$_2$H$_6$, C$_3$H$_8$, and C$_5$H$_{12}$ (neopentane); all angles were kept fixed at 109.47°; standard equilibrium C-H and C-C bond lengths of 1.102 and 1.544 Å, respectively, were uniformly scaled by factors $f$, with $1 \leq f \leq 100$. We concentrated on strong correlations, i.e., restricted our basis set to the single-zeta level ((9s4p)/[2s1p] for C, (4s)/[1s] for H, using subsets of Dunning’s correlation consistent valence double-zeta sets [21]). Since SCF calculations, even with such small basis sets, encounter severe convergence difficulties for large internuclear distances (and yield physically unreasonable energies anyway, high above the dissociation limit), we started from localized two-center orbitals generated as follows. We combined $sp^3$ hybrids on the C centers with each other and with H 1s orbitals to form bonding and anti-bonding LMOs (coefficients $\pm 1$) between next-neighbour atoms; we then Gram-Schmidt-orthogonalized all valence orbitals to the C 1s cores, symmetrically orthogonalized the bonding LMOs among each other, proceeded by Gram-Schmidt-orthogonalizing the anti-bonding LMOs to the bonding ones, and finally symmetrically orthogonalized within the anti-bonding space. With this construction, we can build up an SCF-like closed-shell state, with all bonding LMOs doubly occupied, which should resemble the true SCF ground state of $C_\infty$, in the limit of large cluster size (and in a minimal-basis set rep-
presentation, of course). We then defined groups of orbitals, pairing each of the bonding LMOs with the corresponding anti-bonding one, and performed CASCI calculations [22 - 24] with one of the groups active in turn — this leads to correlation-energy increments $\Delta \epsilon_{CC}$ and $\Delta \epsilon_{CH}$ describing the breaking of a CC or a CH bond in a frozen closed-shell environment. Their sum provides us with a first approximation to the correlation energy of the system, but still not a very good one, since reorganization at the C atoms (leading to $^3P$ ground states in the limit of $R \to \infty$) is not taken into account. We therefore introduced, in the next step, an atomic correction by correlating simultaneously all eight LMOs (bonding and anti-bonding ones) related to a given C atom, in a CASCI calculation. This defines an atomic increment $\Delta \Delta \epsilon_C = \epsilon_C - \sum_i \Delta \epsilon_{CX}$, where $\epsilon_C$ is the correlation energy of the calculation just mentioned, and the $\Delta \epsilon_{CX}$ are the single-bond increments of the neighbouring atoms $X = C, H$. Again, by adding up all $\Delta \Delta \epsilon_C$ contributions, we obtain an improved estimate for the energy of the system. (The next step — which we did not perform any more — would be to determine non-additivity corrections for pairs, triples etc. of atomic increments. In the limit of $n$-tuple corrections ($n \to \infty$), this should lead to the full-CI energy of the system, irrespective of the starting-point chosen, i.e., irrespective of the fact that we did not start from a variational SCF wavefunction.)

In Table 1, the so-obtained correlation-energy estimates for CH$_4$ and C$_2$H$_6$ are compared to reference values (full valence CI results). The errors of the 'SCF' energies are huge, of course ($\sim 1.5$ a.u. for $f = 100$ and $\sim 0.13$ a.u. for $f = 1$, in the case of CH$_4$); about half of the error for $f = 1$ is due to the non-self-consistent preparation of the ground state. Including the bond correlations, $\Delta \epsilon_{CC}$ and $\Delta \epsilon_{CH}$, errors are reduced by nearly an order of magnitude (to $\sim 0.25$ a.u. for $f = 100$ and $\sim 0.02$ a.u. for $f = 1$, in the case of CH$_4$). The atomic correction, $\Delta \Delta \epsilon_C$, corresponds to full CI, in this case,
so we need not discuss it further. It is interesting to note, however, that it also yields the 'exact' result for C\textsubscript{2}H\textsubscript{6} at large distances (i.e., the atoms are properly decoupled to separate ground-state entities), and it deviates by only 1 mH from the full CI value for C\textsubscript{2}H\textsubscript{6} at \( f = 1 \) (using the same basis set). Note that the error of a standard CCSD(T) calculation is of the same order of magnitude, at that internuclear distance, and substantially increases for \( f > 1 \) (~5 mH for \( f = 1.5 \)).

Table 2 gives a compilation of bond increments, \( \Delta \epsilon_{CC} \), and atom increments, \( \Delta \Delta \epsilon_{C} \), for various hydrocarbon molecules, again for a large range of internuclear distances. It is seen that the \( \Delta \epsilon_{CC} \) are fairly stable in various environments; although their absolute value changes by more than two orders of magnitude, the maximum relative change is 3\% between C\textsubscript{2}H\textsubscript{6} and C\textsubscript{5}H\textsubscript{12}. The \( \Delta \Delta \epsilon_{C} \) are less transferable: they are invariant, of course, for \( f = 100 \) as they should, but for \( f = 1 \) the change from four H neighbours (in CH\textsubscript{4}) to a purely C-atom neighbourhood (for the central atom in neopentane) enhances the \( \Delta \Delta \epsilon_{C} \) by nearly a factor of 2. Assuming that changes in the second-nearest neighbour shell do not appreciably modify \( \Delta \Delta \epsilon_{C} \) any more, we can make an estimate for the infinite solid, on the basis of our results. We predict the correlation energy of diamond, \( C_{\infty} \), for our single-zeta basis set, to be \( \sim 4 \Delta \epsilon_{CC}(C_{5}H_{12}) + 2 \Delta \Delta \epsilon_{C}(C_{5}H_{12}) \) per unit cell, and obtain -1.8049, -.9921, -.4681, and -.1286 a.u., for \( f = 100, 2, 1.5, \) and 1, respectively.

It is clear that dynamical correlation effects left out in our example, have significant influence on the properties of diamond, as shown in our previous work \([5,8]\). Therefore, we plan to include such effects, in the future, at the MRCI (or rather MRACPF) level, into our calculations. This would enable a reliable description of the diamond potential-energy surface up to quite large internuclear separations.
IV. SUMMARY AND CONCLUSIONS

We have shown that with the help of multicenter scattering matrices the cumulant wave operator $|\Omega\rangle$ can be constructed even when the electron correlations are strong. The operator $\Omega$ defines the exact ground state. It follows that the corresponding ground-state energy can be calculated in form of increments as previously done for weakly correlated electron systems. The applications described in Section III assumed insulators or semiconductors, because in that case orthonormal localized SCF orbitals can be easily constructed. In principle, however, the scattering matrix approach can be also formulated for nonorthogonal local orbitals. Within the theoretical framework outlined here accurate ground-state wavefunction and energy calculations become feasible. It remains a challenging problem to extend the theory to excited states.
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TABLE I. Energies of an SCF-like initial wavefunction without/with subsequent correlation corrections, $\Delta \epsilon_{IJ}$ and $\Delta \Delta \epsilon_{K}$ (cf. text for definition), as a function of the bond-length scaling factor $f$, in comparison to full-CI calculations (FCI). All energies in Hartree.

|     | SCF       | + $\sum \Delta \epsilon_{IJ}$ | + $\sum \Delta \Delta \epsilon_{K}$ | FCI        |
|-----|-----------|-------------------------------|--------------------------------------|------------|
| a) CH$_4$ |
| $f$ |           |                               |                                      |            |
| 100 | -38.175213 | -39.446762                    | -39.696730                           | —          |
| 2   | -39.260582 | -39.600272                    | -39.760294                           | —          |
| 1.5 | -39.727852 | -39.894261                    | -39.974412                           | —          |
| 1   | -39.990677 | -40.100800                    | -40.122505                           | —          |
| b) C$_2$H$_6$ |
| $f$ |           |                               |                                      |            |
| 100 | -75.661403 | -77.894968                    | -78.394909                           | -78.394909 |
| 2   | -77.493718 | -78.139308                    | -78.485026                           | -78.486933 |
| 1.5 | -78.345506 | -78.647679                    | -78.833566                           | -78.833278 |
| 1   | -78.882457 | -79.059017                    | -79.120651                           | -79.121427 |
TABLE II. Correlation corrections for C-C bonds, $\Delta \epsilon_{CC}$, and atomic re-coupling, $\Delta \Delta \epsilon_C$, for various hydrocarbon molecules, as a function of the bond-length scaling factor $f$, cf. text. All energies in Hartree.

| $f$  | $\Delta \epsilon_{CC}$ | $\Delta \Delta \epsilon_C$ |
|------|-------------------------|-----------------------------|
| 100  | C$_2$H$_6$ | C$_3$H$_8$ | C$_5$H$_{12}$ |
|      | -.326241 | -.326241 | -.326241 |
| 2    | -.138377 | -.138113 | -.137592 |
| 1.5  | -.054767 | -.054566 | -.054178 |
| 1    | -.012927 | -.013081 | -.013386 |

| $f$  | $\Delta \Delta \epsilon_C$ | $\Delta \Delta \epsilon_C$ |
|------|-------------------------|-----------------------------|
| 100  | C$_2$H$_6$ | C$_3$H$_8$ | C$_5$H$_{12}$ |
|      | -.249968 | -.249970 | -.249970 |
| 2    | -.160022 | -.172859 | -.220869 |
| 1.5  | -.080151 | -.092944 | -.125696 |
| 1    | -.021705 | -.030817 | -.037532 |