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Solving the Independent-Particle Model via Nonunitary Transformation Based on Variational Coupled Cluster Singles

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Abstract: We propose an alternative new approach to obtain the Slater determinant ground state solution within an independent-particle approximation using the exponential ansatz for the wave function (Thouless theorem) and exact treatment in terms of variational coupled cluster singles. Although the resulting nonlinear equations formally represent nonterminating expansions, these can be reformulated to finite expansions in terms of the density matrix correction. The latter can be exactly calculated using a very simple recurrence relation within the occupied-occupied block, while the complementary occupied−virtual and virtual−virtual blocks are related and trivially obtained by subsequent matrix multiplications involving the amplitudes of the single-excitation operator. The density matrix is naturally idempotent in any step of the iterative procedure. Blocks of the density matrix are without any further change, apart from the sign, used in the orbital transformation matrix. The latter is not a unitary one, hence leading to nonorthogonal and unnormalized molecular orbitals. These are, however, biorthogonal and can be easily orthonormalized per blocks, if needed in the post-SCF calculations. Formulation is diagonalization free, and the implementation can be easily parallelized. Finally, the formulation provides a challenging way to the solution with "a priori" localized orbitals, a way toward a linear scaling algorithm.

1. Introduction

Recently, we have published a study on the one-particle basis set relaxation effect in the explicitly correlated coupled cluster theory.[1] Our primary goal was to show the error introduced by the assumption of the generalized Brillouin theorem when one uses the explicitly correlated R12-based methods with relatively small main computational (atomic orbital) basis sets. Among others, we have investigated the performance of the traditional coupled cluster singles (CCS) model if one starts from the reference determinant corresponding to a Hartree−Fock (HF) solution with very small (or minimal) basis set, while

in the subsequent CCS calculation the virtual space is created using a much larger basis set. Due to the Thouless theorem,[2] the result should be close to the HF solution with this large basis; nevertheless, it deviates from the correct solution due to the nonvariational nature of the traditional CCS solution. Our observation was that the energies were generally overestimated. Obviously, variational treatment of coupled cluster singles (VCCS) leads to the Hartree−Fock solution, but such an approach gives rise to an infinite expansion of connected terms of the effective Hamiltonian.[3] In an effort to proceed along the truncated expansion in terms of perturbation theory in a generalized sense,[4,5] we discovered that the structure of this expansion enables an effective and exact reformulation in terms of the density correction matrix that can be obtained via simple recurrence relation.[6] Thus, unexpectedly, we arrived at an alternative diagonalization-

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Solving the Independent-Particle Model

J. Chem. Theory Comput., Vol. 6, No. 9, 2010 **2707**

free solution of the HF equations, more generally applicable for any other independent-electron self-consistent-field (SCF) model.

The procedure to solve the SCF model essentially consists of two main steps in each iteration.[7,8] The first step is related to the construction of the effective (density-dependent) Hamiltonian (Fock/KS matrix). This step is not affected by our method. The effort directed toward linear scaling approaches resulted in several techniques applied in different contributions to the Fock/KS matrix.[9–20] In the second step, the density matrix is updated. Conventionally, this matrix is obtained from updated occupied orbitals resulting from the diagonalization of the current Fock/KS matrix (Roothan step[21]). For linearly scaling methods and/or parallelization, the diagonalization is an unwanted step. Two main alternatives to effectively solve this problem have been focused to direct update of the density matrix[7,19,20,22–31] and to directly obtain the localized orbitals.[32–35]

Our method provides an unconventional solution that is based on a nonunitary transformation of the Fock matrix. This solution is surprisingly simple. In section 2, we outline this theory followed by some demonstration of its performance in section 3 and final remarks in section 4.

2. Theory

Let us start from a normalized single reference Slater determinant (Φ) that is related to a basis set of occupied (index i, j, ...) and virtual (index a, b, ...) spin orbitals. For arbitrary orbitals, we shall use indices p, q, ... At the moment, let us assume that this basis is orthogonal. Let

$$\hat{T}_1 = \sum_{i,a} t_a^i a_i^a \qquad (1)$$

be a single-excitation operator with t_a^i being the amplitudes of the particular determinant created by the action of a_i^a on $|\Phi\rangle$. Thouless theorem[2] says that a transformation of the Slater determinant Φ via the action of an exponential operator $e^{\hat{T}_1}$ is again a single Slater determinant. Hence, solution Ψ of any independent-particle model (SCF theory) can be obtained from Φ by finding the amplitudes of $\hat{T}_1$ optimal to the pertinent model.

$$|\Psi\rangle = e^{\hat{T}_1}|\Phi\rangle \qquad (2)$$

This is a long known fact; however, since such ansatz gives rise to a nonunitary transformation, attention has been turned to exponential parametrization leading to unitary transformation, i.e., when the operator in the exponential is antisymmetric.[7] Such a parametrization was successfully applied long ago, e.g., in modern MCSCF and CASSCF algorithms.[36–38]

Direct straightforward use of eq 2 in exact solution within the Hartree−Fock model has been reported in our preliminary conference contribution.[6] This was based on the variational coupled cluster treatment, which has led to very simple final equations, which naturally avoid the diagonalization step. Here, we recapitulate the derivation in a different perspective.

2.1. One Particle Density Matrix. We shall show later that the density matrix plays the key role in the exact solution using ansatz eq 2. Its parts constitute the building blocks for all the (nonunitary) transformation matrices leading to the exact solution for the pertinent model. Matrix elements of the one particle density matrix (**D**) expressed in the reference basis and using the ansatz of eq 2 are given as

$$D_p{}^q = \frac{\langle\Phi|e^{\hat{T}_1^\dagger}a_p^q e^{\hat{T}_1}|\Phi\rangle}{\langle\Phi|e^{\hat{T}_1^\dagger}e^{\hat{T}_1}|\Phi\rangle} \qquad (3)$$

As it was shown over 40 years ago by Čížek,[3] this expectation value of the replacement operator a_p^q can be expressed in an infinite expansion of connected terms:

$$D_p^q = \langle\Phi|a_j^i|\Phi\rangle\delta_i^q\delta_p^j + \langle\Phi|(e^{\hat{T}_1^\dagger}\tilde{a}_p^q e^{\hat{T}_1})_C|\Phi\rangle \qquad (4)$$

where $\tilde{a}_p{}^q$ is a normal ordered replacement operator with respect to Φ. The first term represents elements of the reference density matrix ($\mathbf{D}^{ref}$), which is in our basis the unity matrix in the occupied−occupied (oo) block. The second term represents correction to this reference density. For nonzero $\hat{T}_1$ also the virtual−virtual (vv) and occupied−virtual (ov) blocks of **D** are nonzero. Let the density correction matrix be **X**. Then

$$\mathbf{D} = \begin{pmatrix} \mathbf{1}_{oo} + \mathbf{X}_{oo} & \mathbf{X}_{ov} \\ \mathbf{X}_{vo} & \mathbf{X}_{vv} \end{pmatrix} \qquad (5)$$

2.1.1. Relations between the Density Matrix Sub-Blocks. In a spin−orbital basis matrix of eq 5 is idempotent. $\mathbf{D} = \mathbf{DD}$ implies that the individual blocks are related as follows:

$$\mathbf{X}_{oo} = -\mathbf{X}_{oo}\mathbf{X}_{oo} - \mathbf{X}_{ov}\mathbf{X}_{vo} \qquad (6)$$

$$\mathbf{X}_{vv} = \mathbf{X}_{vv}\mathbf{X}_{vv} + \mathbf{X}_{vo}\mathbf{X}_{ov} \qquad (7)$$

$$\mathbf{X}_{vv}\mathbf{X}_{vo} = -\mathbf{X}_{vo}\mathbf{X}_{oo} \qquad (8)$$

$$\mathbf{X}_{ov}\mathbf{X}_{vv} = -\mathbf{X}_{oo}\mathbf{X}_{ov} \qquad (9)$$

Each matrix element of **X** represents an infinite expansion. We naturally assume that $\hat{T}_1^\dagger$ is a true Hermitian conjugate of $\hat{T}_1$ and hence for real amplitudes $t_i^a = t_a^i$. First terms in the aforementioned expansions are given by $\mathbf{t}$ ($\mathbf{t}^T$) for the ov (vo) blocks, whereas in oo and vv blocks the initial terms arise from single contractions of $\hat{T}_1^\dagger$ with $\hat{T}_1$ via the virtual orbital index resulting in

$$\mathbf{x}_{oo} = -\mathbf{t}\mathbf{t}^T \qquad (10)$$

or via the occupied orbital index resulting in

$$\mathbf{x}_{vv} = -\mathbf{t}^T\mathbf{t} \qquad (11)$$

Using diagrammatic technique it is easy to show that[6]

$$X_{oo} = \sum_{n=1}^{\infty} x_{oo}^n \qquad (12)$$

$$X_{vv} = -\sum_{n=1}^{\infty} x_{vv}^n \qquad (13)$$

(Note that in ref 6 we used opposite signs for the oo and vv blocks of **X**, since the matrix has been related to the density correction operator.)

Off diagonal blocks can be easily calculated as

$$X_{ov} = X_{vo}^T = t + X_{oo}t = D_{oo}t = t - tX_{vv} \qquad (14)$$

and vice versa the diagonal blocks are related to off-diagonal ones by simple relations:

$$X_{vv} = X_{vo}t \qquad (15)$$

$$X_{oo} = -tX_{vo} \qquad (16)$$

Identities of eqs 6–9 equivalently follow from eqs 10–14. It underlines the fact that the density matrix derived from the wave function of eq 2 is naturally idempotent without imposing this property. Moreover, it is easy to show that this matrix also fulfills the trace relation

$$Tr(D) = N_{el} \qquad (17)$$

If we define

$$y_k = t^T x_{oo}^k = x_{vv}^k t \qquad (18)$$

Equations 12 and 13 can be equivalently rewritten as

$$X_{oo} = -\sum_{k=0}^{\infty} (y_k y_k^T + y_k y_{k+1}^T) \qquad (19)$$

$$X_{vv} = \sum_{k=0}^{\infty} (y_k^T y_k + y_k^T y_{k+1}) \qquad (20)$$

Since, obviously, for any k, l

$$Tr(y_k y_l^T) = Tr(y_k^T y_l) \qquad (21)$$

and consequently

$$Tr(X_{oo}) = -Tr(X_{vv}) \qquad (22)$$

$$Tr(D) = Tr(D^{ref}) = N_{el} \qquad (23)$$

2.1.2. Obtaining the Density Matrix. The density matrix form of eq 5 is only relevant when eqs 12 and 13 are convergent series. This is true if the eigenvalues of the x_{oo} matrix are contained in the interval $(-1,0)$, and similarly, eigenvalues of the x_{vv} matrix are from $(0,1)$. Consequently, the values of **t**-amplitudes must be from $(-1,1)$. This also means that the reference determinant must dominate, since its weight in the wave function expansion is unity. Sufficiently good reference is usually achieved using a SCF start from a very small basis or simplified models. Convergence

in these expansions is quadratic in **t** and, in addition, it is accelerated by the alternating sign of the individual contributions. Equation 14 shows that the sub-blocks of **X** are related and, consequently, only that of X_{oo} or X_{vv} needs to be evaluated via the infinite expansion.

Equations 5 and 12 imply that

$$X_{oo} = D_{oo}x_{oo} \qquad (24)$$

and subsequently from eq 5

$$D_{oo} = 1_{oo} + D_{oo}x_{oo} \qquad (25)$$

Equation 25 suggests a recurrence relation to calculate D_{oo}:

$$D_{oo}^{(k+1)} = 1_{oo} + D_{oo}^{(k)}x_{oo} \qquad (26)$$

starting with

$$D_{oo}^{(0)} = 1_{oo} \qquad (27)$$

Alternatively, the D_{oo} block can be evaluated from eq 25 as

$$D_{oo} = (1 - x_{oo})^{-1} \qquad (28)$$

Though matrix inversion is not our preferred operation, the latter evaluation of D_{oo} might be useful when the recurrence of eq 26 converges very slowly. However, using eq 28 would be unphysical when eq 12 is divergent, as pointed out at the beginning of this section.

Calculation of the remaining blocks of **D** easily follows from eqs 14 and 15. It is not the purpose of this paper to deal with the Fock matrix (**F**) construction. Having updated **D** and/or subsequently the electron density, this can be performed using established procedures in DFT or Hartree−Fock methods.

2.2. Orbital Transformation Matrix. For this moment, let us assume that we have the Fock matrix in the original reference molecular orbital basis and hence the Fock operator

$$\hat{F} = \sum_{p,q} F_p^q a_q^p \qquad (29)$$

In fact, $\hat{F}$ can be replaced by any generic independent-particle operator. The expectation value of this operator in the wave function of eq 2 reads

$$\frac{\langle \Phi | e^{\hat{T}_1^\dagger} \hat{F} e^{\hat{T}_1} | \Phi \rangle}{\langle \Phi | e^{\hat{T}_1^\dagger} e^{\hat{T}_1} | \Phi \rangle} = \sum_{p,q} F_q^p \frac{\langle \Phi | e^{\hat{T}_1^\dagger} a_p^q e^{\hat{T}_1} | \Phi \rangle}{\langle \Phi | e^{\hat{T}_1^\dagger} e^{\hat{T}_1} | \Phi \rangle} = Tr[FD(t^T, t)] \qquad (30)$$

Making this expectation value stationary with respect to the amplitudes of $\hat{T}_1^\dagger$ (or equivalently $\hat{T}_1$) gives rise to equations determining **t**. In this step, **F** can be treated as fixed and independent from **t**. Thus, our task is reduced to solve for

$$0 = \sum_{p,q} F_q^p \frac{\partial D_p^q}{\partial t_i^a} \qquad (31)$$

Differentiating the oo block of **D** using eqs 10 and 12 gives rise to

Solving the Independent-Particle Model

J. Chem. Theory Comput., Vol. 6, No. 9, 2010 **2709**

$$\sum_{k,l}^{occ} F_l^{\,k} \frac{\partial D_k^l}{\partial t_i^a} = -\sum_{k,l}^{occ} \sum_{n=0}^{\infty} \sum_{m=0}^{n} (\mathbf{x}_{oo}^{n-m})_k^i F_l^{\,k} (\mathbf{x}_{oo}^m \mathbf{t})_a^l \quad (32)$$

This expression can be rearranged in a way that one clearly identifies blocks of the density matrix. Afterward, the rhs of eq 32 can be rewritten in a more compact matrix form using these blocks as

$$-(\mathbf{1}_{oo} + \sum_{n}^{\infty} \mathbf{x}_{oo}^n)\mathbf{F}_{oo}(\mathbf{1}_{oo} + \sum_{m}^{\infty} \mathbf{x}_{oo}^m)\mathbf{t} =$$
$$-(\mathbf{1}_{oo} + \mathbf{X}_{oo})\mathbf{F}_{oo}\mathbf{X}_{ov} = -\mathbf{D}_{oo}\mathbf{F}_{oo}\mathbf{D}_{ov} \quad (33)$$

Similarly, for the remaining three blocks of the density using eqs 10−14 we arrive at

$$\sum_{k}^{occ} \sum_{c}^{vir} F_c^{\,k} \frac{\partial D_k^c}{\partial t_i^a} = \sum_{k}^{occ} \sum_{c}^{vir} \sum_{n=0}^{\infty} \sum_{m=0}^{n} (\mathbf{x}_{oo}^m)_k^i F_c^{\,k} (\mathbf{x}_{vv}^{n-m})_a^c \quad (34)$$

$$\sum_{k}^{occ} \sum_{c}^{vir} F_k^{\,c} \frac{\partial D_c^k}{\partial t_i^a} = -\sum_{k}^{occ} \sum_{c}^{vir} \sum_{n=0}^{\infty} \sum_{m=0}^{n} (\mathbf{t}\mathbf{x}_{vv}^{n-m})_c^i F_k^{\,c} (\mathbf{x}_{oo}^m \mathbf{t})_a^k$$
$$(35)$$

$$\sum_{c,d}^{vir} F_c^{\,d} \frac{\partial D_d^c}{\partial t_i^a} = \sum_{c,d}^{vir} \sum_{n=0}^{\infty} \sum_{m=0}^{n} (\mathbf{t}\mathbf{x}_{vv}^{n-m})_d^i F_c^{\,d} (\mathbf{x}_{vv}^m)_a^c \quad (36)$$

From eqs 32−36 follows the matrix form of eq 31:

$$(\mathbf{1}_{oo} + \mathbf{X}_{oo})[\mathbf{F}_{ov}(\mathbf{1}_{vv} - \mathbf{X}_{vv}) - \mathbf{F}_{oo}\mathbf{X}_{ov}] +$$
$$\mathbf{X}_{ov}[\mathbf{F}_{vv}(\mathbf{1}_{vv} - \mathbf{X}_{vv}) - \mathbf{F}_{vo}\mathbf{X}_{ov}] = \tilde{\mathbf{F}}_{ov} = 0 \quad (37)$$

This equation can be also written as

$$(\mathbf{DF} - \mathbf{DFD})_{ov} = (\mathbf{D}[\mathbf{D}, \mathbf{F}])_{ov} = 0 \quad (38)$$

and is equivalent to the Brillouin theorem.

Equation 37 represents a part of a more general transformation of the (actual) Fock operator expressed in the reference basis to a basis in which ov (vo) block is zero, in other words, to a basis in which the Brillouin theorem holds (at least with the current fixed **F**):

$$\tilde{\mathbf{F}} = \mathbf{Q}^{\mathrm{T}}\mathbf{F}\mathbf{Q} \quad (39)$$

The transformation matrix (**Q**) can be easily extracted from eq 37:

$$\mathbf{Q} = \mathbf{1} + \begin{pmatrix} \mathbf{X}_{oo} & -\mathbf{X}_{ov} \\ \mathbf{X}_{vo} & -\mathbf{X}_{vv} \end{pmatrix} \quad (40)$$

Transformation as in eq 39 is not a unitary one. Taking into account eqs 6−9 one can easily show that

$$\mathbf{Q}^{\mathrm{T}}\mathbf{Q} = \mathbf{1} + \begin{pmatrix} \mathbf{X}_{oo} & 0 \\ 0 & -\mathbf{X}_{vv} \end{pmatrix} \quad (41)$$

which is different from the unity matrix for $\mathbf{X}_{oo} \neq 0$. Moreover, $Tr(\mathbf{Q}^{\mathrm{T}}\mathbf{Q}) = N + 2Tr(\mathbf{X}_{oo})$ (cf. eq 22) is also different from the number of orbitals. This means that the molecular orbitals (**C**) that are obtained from the reference basis ($\mathbf{C}^{\mathrm{ref}}$) as

$$\tilde{\mathbf{C}} = \mathbf{C}^{\mathrm{ref}}\mathbf{Q} \quad (42)$$

are not orthogonal within the individual occupied and virtual blocks. Moreover, these orbitals are not normalized even when the reference orbitals were normalized. The occupied and virtual blocks are biorthogonal; i.e., when **S** is the overlap matrix in the initial generally nonorthogonal computational basis, then

$$\tilde{\mathbf{C}}_o^{\mathrm{T}}\mathbf{S}\tilde{\mathbf{C}}_v = 0 \quad (43)$$

Let us stress, however, that the "new" molecular orbitals (eq 42) need not be ever constructed. Their construction is fully optional for the post-SCF purpose. Using eq 41 one can immediately construct a unitary transformation matrix as

$$\mathbf{U} = \begin{pmatrix} (\mathbf{1}_{oo} + \mathbf{X}_{oo})^{1/2} & -\mathbf{X}_{ov}(\mathbf{1}_{vv} - \mathbf{X}_{vv})^{-1/2} \\ \mathbf{X}_{vo}(\mathbf{1}_{oo} + \mathbf{X}_{oo})^{-1/2} & (\mathbf{1}_{vv} - \mathbf{X}_{vv})^{1/2} \end{pmatrix} \quad (44)$$

and hence the final orthonormal set (**C**) of molecular orbitals:

$$\mathbf{C}_o = \mathbf{C}^{\mathrm{ref}}(\mathbf{Q}_{oo} + \mathbf{Q}_{vo})\mathbf{Q}_{oo}^{-1/2} \quad (45)$$

$$\mathbf{C}_v = \mathbf{C}^{\mathrm{ref}}(\mathbf{Q}_{vv} + \mathbf{Q}_{ov})\mathbf{Q}_{vv}^{-1/2} \quad (46)$$

Note that in order to solve the problem, we as well never need the whole Fock matrix in the "updated orbital basis", merely its ov block $\tilde{\mathbf{F}}_{ov}$ (cf. eq 37), which is obtained in a two-step matrix multiplication formally scaling as $N_o N^2 + N_o N_v N$, where N, N_o, and N_v are the number of basis functions, the number of occupied, and the number of virtual orbitals, respectively.

Let us recall that the energy is calculated using the correctly normalized density matrix of eq 5 as an expectation value of the Hamiltonian.

2.3. Updating t-Amplitudes. In principle, there is no explicit need to update the amplitudes, since one can get the solution for **X** (and hence update the density) using the set of nonlinear equations resulting from eqs 37, 6, and 7. A much simpler approach, and algorithmically much more favorable, is to evaluate **t** and subsequently the $\mathbf{X}_{oo}$ matrix using eqs 10 and 25 from which the $\mathbf{X}_{ov}$ and $\mathbf{X}_{vv}$ blocks are easily obtained via eqs 14 and 15.

Indeed, in terms of **t**, eq 37 can be rewritten as

$$\mathbf{f}_{ov} + \mathbf{t}\mathbf{f}_{vv} - \mathbf{f}_{oo}\mathbf{t} + \text{higher order terms in } \mathbf{t} = 0 \quad (47)$$

We denote by **f** the original Fock matrix in the reference basis constructed by using the pertinent reference density. Moving the terms with diagonal elements of **f** in eq 47 to the rhs suggests the **t** in the $(k + 1)$ iteration as

$$t_a^{i(k+1)} = t_a^{i(k)} + \tilde{F}_a^{i(k)}/(f_i^i - f_a^a) \quad (48)$$

With the initial $t_a^{i(0)} = 0$ we have

$$t_a^{i(1)} = f_a^i/(f_i^i - f_a^a) \quad (49)$$

Both the density from which the Fock matrix was calculated and the transformation matrix **Q** are functions of the same $\mathbf{t}^{(k)}$; i.e. $\tilde{\mathbf{F}}^{(k)} \equiv \tilde{\mathbf{F}}(\mathbf{t}^{(k)})$. Hence, a one-step update

due to eq 48 is fully appropriate and leads to a balanced treatment such as that used in established coupled cluster algorithms.

Alternatively, one could solve eq 48 in a subiterative procedure with $\mathbf{F}^{(k)}$ being fixed, while merely updating the $\tilde{\mathbf{F}}_{ov}$ via eq 39 until the convergence of $\mathbf{t}$ in the given macroiteration. We have experimented in this way. However, it turned out that the convergency of the global iterative process worsened, which suggests that such a procedure not be recommended.

2.4. Algorithm Summary. The key new aspects of this theory are (i) a facile recurrence relation of eq 35 to update the one particle density, (ii) a simple update of the **t**-amplitudes via eq 48, which replaces the diagonalization step, and (iii) nonunitary transformation of eq 39. The main attractive feature is that the transformation matrix $\mathbf{Q}$ (eq 40) is easily constructed from parts of the density matrix $\mathbf{D}$ (eq 5) without additional (relevant) computational demand. These features give rise to an efficient and simple algorithm that can be implemented in any existing code by simple modifications:

Init (k = 0). Create the reference (initial) orbitals and the initial Fock matrix ($\mathbf{F}^{(0)} = \mathbf{f}$). It is not necessary from the principle, but it improves the convergence when one starts from semicanonical orbitals.[39]

Step 1 (k = k + 1). Calculate $\mathbf{t}^{(k)}$ according to eq 48.

Step 1a. When appropriate, apply DIIS[40] to **t** amplitudes.

Step 2. Calculate $\mathbf{x}_{oo}$ (eq 10) and $\mathbf{D}_{oo}$ using eq 25, $\mathbf{X}_{ov}$ using eq 14, and $\mathbf{X}_{vv}$ using eq 15. Complete the density matrix $\mathbf{D}^{(k)}$ (eq 5) and the transformation matrix $\mathbf{Q}^{(k)}$ (eq 40).

Step 3. Calculate $\mathbf{F}^{(k)} \equiv \mathbf{F}^{(k)}(\mathbf{D}^{(k)})$ related to the chosen independent particle model. In most algorithms, this step is performed in AO basis and a transformation of the density matrix to the latter basis precedes this step. Optionally, at this step calculate the energy and go to the final step if converged.

Step 4. Create $\tilde{\mathbf{F}}_{ov}^{(k)}$ using (partial) transformation of eq 39. If $\|\tilde{\mathbf{F}}_{ov}^{(k)}\| >$ threshold, go to step 1.

Final. Calculate the energy from the resulting density and if necessary construct the molecular orbitals using eqs 45 and 46.

2.5. Discussion. Our approach does not affect the calculation of the Fock matrix. It provides a simple alternative to existing methods that replace the "traditional" diagonalization step of the Fock matrix in which the molecular orbitals are updated. Certainly, several common features can be found in these methods. Indeed, quite a similar central equation as our eq 37 appears also in exact reformulation of the diagonalization step using Cayley-type parametrization of the unitary matrix by Liang and Head-Gordon.[28] As follows from the preceding section, our approach also provides an exact reformulation of this problem. Consequently, the updated density matrix naturally obeys the trace relation and is idempotent without subsequent purification. The latter is needed in approaches that use a truncated parametrical expansion of the density matrix such as that used in the recent augmented Roothan-Hall method.[31]

We deviate from other methods from the beginning by working with a wave function that is not normalized. The exponential ansatz of the wave function is naturally related to the infinite expansion of the density matrix that can be exactly calculated using the recurrence formula of eq 26.

Instead, in the method of Liang and Head-Gordon, this step requires an inversion of a matrix equally in the oo block. It would be inappropriate to compare the "theoretical" count of multiplications in the aforementioned methods, as this number varies in solving the set of nonlinear equations similar to eq 37. An alternative to solving this equation is in our method provided by a simple update of the **t** amplitudes via dividing the ov block of the Fock matrix by orbital energy denominator. If needed for a better convergence, e.g., when the (reference) HOMO is very close to LUMO, there is a space here to apply a denominator shift.

Eventually, used exponential ansatz can be effectively combined with a Newton method, since the exact second derivative of the density matrix with respect to **t** nicely factorizes. In terms of $\mathbf{Q}$ we have (eqs 32−36):

$$(\delta_k^q + \delta_c^q)\frac{\partial D_q^p}{\partial t_i^a} = (\delta_k^q + \delta_c^q)\frac{\partial X_q^p}{\partial t_i^a} = (\delta_k^q - \delta_c^q)Q_q^i Q_a^p \quad (50)$$

$$\frac{\partial^2 D_q^p}{\partial t_i^a t_j^b} = Q_q^i Q_a^j Q_b^p + Q_q^j Q_a^i Q_b^p \quad (51)$$

3. Sample Calculations

The correctness of our approach has been numerically checked and proven already in our preliminary paper.[6] Its performance is here demonstrated using the Hartree−Fock SCF approach for four systems including uracil, a complex of four guanine molecules, a dimer of two hydrocarbon chains $(C_{18}H_{38})_2$, and a complex of $C_{54}H_{18}$ sheet with cytosine−guanine pair. These systems range from 12 to 112 atoms and the number of occupied orbitals varies from $N_o = 29$ for uracil to $N_o = 239$ for the last mentioned complex.

We have tested starts from various (reference) wave functions including simplified models (such as EHT or LDA approximations), small or minimal atomic orbital basis subsets, and/or a combination of both. When we started from a basis set smaller than the target computational basis set, i.e., from its subset, the virtual subspace was completed by Schmidt orthogonalizing the complementary atomic orbitals to the MO's resulting from the small initial basis. Semicanonical orbitals[39] were finally created by separate diagonalization of the oo and vv block of the Fock matrix obtained using the initial density matrix. These semicanonical orbitals served as our reference basis. At this stage, we have not investigated alternative reference bases that would eventually not require a diagonalization step.[41] Without any further investigation and optimization, we have used the DIIS procedure applied to the **t** amplitudes, always from the three subsequent iterations.

Results are summarized in Table 1. Geometries are available in the Supporting Information and additional computational details are as follows:

Solving the Independent-Particle Model

J. Chem. Theory Comput., Vol. 6, No. 9, 2010 **2711**

Table 1. Performance of the Proposed Theory for Selected Molecular Systems[a]

initial MOS[b]	ΔE_{ini}[c]	$\Delta E_{ini} + E^{(2)}$ [d]	max(**t**)	it$_{rec}$[e]	it$_{SCF}$[f]
uracil: aug-cc-pV5Z, $N = 1336$, $N_o = 29$, $E_{HF} = -412.655\ 211$					
EHT 2s1p/1s	2.031 453	−0.523 032	0.1327	14/22	21/26
($N = 44$)					
LDA 2s1p/1s	0.942 645	0.117 791	0.1067	5/8	9/16
HF 2s1p/1s	0.890 455	0.072 809	0.0672	5/7	9/16
$(C_{18}H_{38})_2$: 6-31G**, $N = 884$, $N_o = 146$, $E_{HF} = -1407.668\ 375$					
EHT 2s1p/1s	23.596 339	1.020 783	0.2871	10/15	7/11
($N = 256$)					
LDA 2s1p/1s	20.750 178	−0.064 462	0.2770	12/18	8/11
HF 2s1p/1s	20.566 948	0.612 301	0.2937	11/17	7/11
EHT 6-31G**	6.482 139	−0.255 941	0.2066	6/10	7/11
(guanine)$_4$: 6-31G**, $N = 716$, $N_o = 156$, $E_{HF} = -2157.142\ 890$					
EHT 6-31G	9.418 091	−0.965 297	0.1172	10/15	17/24
($N = 436$)					
LDA 6-31G	0.887 659	0.144 224	0.0798	4/6	9/16
HF 6-31G	0.479 354	0.059 236	0.0361	4/6	7/11
EHT 6-31G**	9.591 119	−1.052 849	0.1189	10/16	17/24
$[(C_{54}H_{18})-(cytosine-guanine)]$: $N_o = 239$					
aug-cc-pVDZ/aug-cc-pVDZ-RI, $N = 1931$, $E_{HF} = -2988.139\ 195$					
EHT 2s1p/1s	11.312 142	−0.336 064	0.1216	9/14	17/28
($N = 393$)					
HF 2s1p/1s	5.761 793	0.424 057	0.0401	6/8	13/20
HF 3s2p/2s	1.300 318	0.146 213	0.0199	4/6	9/18
($N = 713$)					
aug-cc-pVTZ/aug-cc-pVTZ-RI, $N = 4002$, $E_{HF} = -2988.686\ 645$					
EHT 2s1p/1s	11.571 240	−0.359 279	0.1262	9/14	17/20
HF 2s1p/1s	6.002 295	0.417 410	0.0464	6/8	13/16
HF 4s3p/3s	1.493 402	0.172 046	0.0145	4/6	9/12
($N = 1033$)					

[a] Energies are in E_h. [b] Approximation and basis set used to obtain the initial MOS. [c] $\Delta E_{ini} = E_{ini} - E_{HF}$; $E_{ini} = \langle \Phi | \hat{H} | \Phi \rangle$. [d] $E^{(2)}$ according to eq 52. [e] Number of recurrence cycles to converge the norm of $\mathbf{D}_{oo}$ (eq 26) residual below $10^{-6}/10^{-10}$. [f] Number of SCF iterations a/b; a: HF energy threshold 10^{-6}; b: residual **t** norm threshold 10^{-5}, for aug-cc-pVTZ 10^{-4}.

Uracil: we have used the geometry of the neutral molecule as in a recent paper by Bachorz and Klopper.[42] Here, we employed relatively extensive aug-cc-pV5Z,[43-45] whereas the initial basis was a minimal one. 2s1p for a non-hydrogen atom and 1s for hydrogen correspond to the first contracted functions (with highest exponents) from the cc-pV5Z[43] set, pertinent to the given angular momentum.

$(C_{18}H_{38})_2$: a complex of two parallel linear C_{18} alkane chains[46] was calculated with the 6-31G** basis.[47,48] The minimal 2s1p/1s basis used for constructing the initial orbital set was again the subset of the main 6-31G** basis including contracted functions with the largest exponents.

(Guanine)$_4$: a planar complex of four guanine molecules[49] was calculated using 6-31G** with special polarization functions with d-exponent 0.25 for non-hydrogen atoms and p-exponent 1.1 for hydrogen atoms.[50]

$[(C_{54}H_{18})-(cytosine-guanine)]$ (a stacking van der Waals complex of a graphene sheet with a DNA base pair):[46] We show performance of our method using aug-cc-pVDZ and aug-cc-pVTZ basis sets. In these cases, the Fock matrix calculation has been performed using the RI (density fitting)

approach using the fitting sets of Weigend et al.[51] Initial basis sets are subsets of the full sets, similarly as aforementioned.

In Table 1 we focus on the following quantities:

a Deviation of the energy corresponding to the initial guess E_{ini} from the exact (final) HF energy in the given basis, which is one of the measures that reflect the quality of the reference orbital basis.

b Deviation of the energy using a simple second-order energy correction from first order **t**, $E_{ini} + E^{(2)}$. This correction is given by a simple formula:

$$E^{(2)} = \sum_{i,a} (f_i^a)^2/(f_i^i - f_a^a) \qquad (52)$$

c The largest **t**-amplitude, which is a different measure of the deviation of the reference orbital basis from optimal molecular orbitals.

d The number of microiterations needed to converge the recurrence relation eq 26. Since this step includes matrix multiplications only over the oo block, the timing is typically negligible compared to the timing of the whole iteration step.

e The number of (macro)iterations using different thresholds to stop the convergence process.

One observes that initial orbitals stemming from minimal (or very small) basis sets were more than appropriate in order to achieve a smooth convergence. As the largest **t**-amplitudes demonstrate, the initial reference states were often quite far from the exact solution. The number of needed iterations both in the recurrence cycle and the outer loop loosely correlates with the error of the initial energy of the reference state and hence with the value of the largest **t**-amplitude. The EHT start seems to perform somewhat worse than HF or LDA.

As far as the recurrence iterations are concerned, one has to keep in mind that these involve matrix multiplications with the dimension of the number of occupied orbitals, i.e., the timing is practically negligible. For the least favorable case from our examples, (guanine)$_4$, the recurrence cycle represents less than 1% of the computational costs for matrix multiplication with the full basis. In all other examples, this fraction is still less by one or more orders of magnitude.

The column with the simple second-order energy correction is given here just for curiosity. Although it recovers most of the initial energy error in absolute value, this correction is still unreliable and, as seen, is hardly predictable mainly due to its nonvariational nature.

We add a short remark related to the convergence behavior of the suggested algorithm for basis sets exhibiting significant linear dependence. Indeed, the complex of the graphene sheet with the DNA base pair calculated with the aug-cc-pVTZ basis represents such a case and has been suggested to us as a really difficult one. The condition number for the overlap matrix is on the order of 10^{13}. Even without eliminating any functions from this ill-conditioned set, a smooth convergence has been achieved, though, as noted in Table 1, the numerical accuracy of the final **t**-amplitudes has been little bit worsened. Nevertheless, an error of 10^{-4} in the norm of **t** still guaranties that the density matrix is sufficiently converged to about 10^{-8}.

4. Conclusions

We have shown that an effective alternative way of solving the independent particle problem without diagonalization is provided by an exact solution using a variational coupled cluster singles treatment. The formal nonterminating expansion of connected terms in the resulting energy expression can be reformulated to finite expansion in terms of the density matrix correction. The latter can be exactly calculated using a very simple recurrence relation within the occupied−occupied block, while the complementary occupied−virtual and virtual−virtual blocks are related and trivially obtained by subsequent matrix multiplications involving the amplitudes of the single-excitation operator. The density matrix is naturally idempotent in any step of the iterative procedure. As well, the trace relation is satisfied at each step.

Differentiation of the energy with respect to the amplitudes of the single excitation operator leads to nonunitary transformation of the Fock matrix, however, by removing the occupied−virtual block, i.e., transforming to a basis in which the Brillouin theorem is satisfied. Such transformation leads to an unnormalized and nonorthogonal, though still biorthogonal, set of molecular orbitals. The transformation matrix is built from blocks of the density matrix without any further change, apart from the sign. If needed, final molecular orbitals are easily obtained by a simple separate orthogonalization for the occupied and virtual block.

An advantage of the present formulation is a fact that the nonlinear eq 37 does not need to be explicitly solved in each iteration, instead a simple update of the amplitudes serves well. This leads to a balanced treatment when the density and the transformation matrix are always constructed from the same amplitudes.

Since the formulation is diagonalization free, the main parallelization bottleneck is overcome. If we do not comment on the construction of the Fock matrix, the rest is fully driven by matrix multiplications and can be effectively parallelized. In the simplest case, just the parallel BLAS subroutines are used. Finally, the formulation provides a challenging way to the solution with "a priori" localized orbitals, a way toward linear scaling algorithm.

Our pilot results are very promising and confirm that implementation of the present approach into an efficient large-scale production code might be worth of considering.

Supporting Information Available: Geometries for the systems discussed. This material is available free of charge via the Internet at http://pubs.acs.org.

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Solving the Independent-Particle Model

J. Chem. Theory Comput., Vol. 6, No. 9, 2010 **2713**

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