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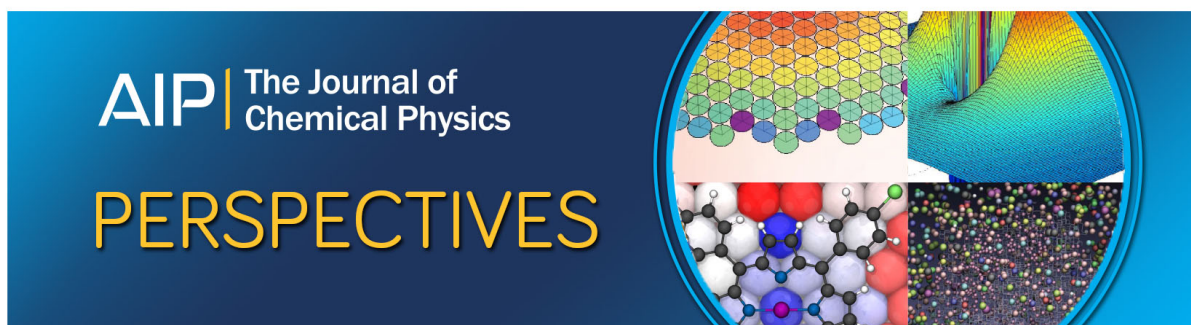
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# A comparison between the Møller–Plesset and Green's function perturbative approaches to the calculation of the correlation energy in the many-electron problem

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The well-known expression for the total energy in terms of the single-particle many-body Green's function is analyzed in detail. In particular the relation between the  $n$ th order Møller–Plesset energy and the energy calculated from a Green's function generated by the  $n$ th order self-energy is investigated. It is shown how the  $n$ th order Møller–Plesset energy can be expressed in terms of the Green's function. The  $H_2$  molecule is studied in a minimal basis to serve as a model in which exact results can be easily obtained. Numerical calculations are performed for  $H_2$ , He, Be, LiH, Ne, HF,  $H_2O$ ,  $NH_3$ , and  $CH_4$  and the results are analyzed in detail.

## I. INTRODUCTION

The Green's function (GF) theory provides a viable approach to the many-electron problem. From the broad range of applications<sup>1–5</sup> we mention only the calculation of ionization potentials,<sup>6,7</sup> and the correlation energy.<sup>8,9</sup> In this paper we concentrate on the correlation energy. Since, as usually implemented, the GF method is essentially a perturbative method like Møller–Plesset theory, the question arises what exactly the relation is between these two methods.

The lowest order Møller–Plesset theory, usually denoted as MP(2), is simple and the corresponding second order energy correlation, denoted as  $E^{(2)}$ , can easily be obtained after an SCF calculation has been completed. The lowest order Green's function theory, commonly referred to as second order Green's function theory, and denoted as GF(2) on the other hand is more elaborate. The second order self-energy matrix  $\Sigma^{(2)}$  has to be obtained in a number of points in the complex plane after which the second order Green's function, denoted as  $G^{\text{Dyson}(2)}(\omega)$ , can be obtained by matrix inversion. The advantage is that  $G^{\text{Dyson}(2)}(\omega)$  contains contributions from second up to infinite order in the self-energy. The total energy obtained from  $G^{\text{Dyson}(2)}(\omega)$  is denoted as  $E^{\text{Dyson}(2)}$ .

In order to facilitate a comparison between  $E^{\text{Dyson}(2)}$  and  $E^{(2)}$  a detailed analysis of the expression for the total energy in terms of an order parameter  $\lambda$  is performed. It is shown that the  $n$ th order contribution to the total energy involves the strictly  $n$ th and  $(n-1)$ th order contributions to the full Green's function, which are not the same as the Green's functions calculated from the  $n$ th and  $(n-1)$ th order self-energy.

Since the first order Green's function vanishes because the Fock operator is taken as the zero order Hamiltonian, the second order Møller–Plesset energy  $E^{(2)}$  can be expressed in terms of the second order contribution to the Green's function only. The expression of the MP(2) energy  $E^{(2)}$  in terms of the Green's function allows comparison with the second order Green's function energy  $E^{\text{Dyson}(2)}$ —which contains higher order contributions.

To further analyze the relation between Møller–Plesset and Green's function theory a simple model is studied in which all quantities can be worked out in detail: the minimal basis  $H_2$  molecule. In this model the exact Green's function can be obtained from the Feynman–Dyson amplitudes. From these one can obtain the exact self-energy. This is particularly interesting in the limit of infinitely separated hydrogen nuclei. If one calculates the second order self-energy in this limit it turns out to be identical to the exact self-energy. Now both  $E^{(2)}$  and  $E^{\text{Dyson}(2)}$  are calculated from this second order self-energy but in this special case  $E^{(2)}$  diverges and  $E^{\text{Dyson}(2)}$  becomes exact. This very different behavior is a direct consequence of the Dyson summation: the inclusion of terms up to infinite order in the Green's function is crucial in avoiding the divergencies. Following this model study the results of numerical calculations on a number of molecules are reported, i.e.,  $H_2$ , He, Be, LiH and the ten-electron series Ne, HF,  $H_2O$ ,  $NH_3$ ,  $CH_4$ .

## II. THEORY

In all perturbative approaches to the calculation of the correlation energy a partitioning of the Hamiltonian into a solvable zero order part and a perturbative or interaction part is the starting point. Thus we write<sup>10,11</sup>

$$\begin{aligned} \hat{H}(\lambda) = & \int dx_1 \psi^\dagger(x_1) h(x_1) \hat{\psi}(x_1) + \int dx_1 dx'_1 \hat{\psi}^\dagger(x'_1) v^{\text{HF}}(x'_1, x_1) \hat{\psi}(x_1) \\ & + \lambda \left[ \frac{1}{2} \int dx_1 dx_2 \hat{\psi}^\dagger(x_1) \hat{\psi}^\dagger(x_2) V(x_1, x_2) \hat{\psi}(x_2) \hat{\psi}(x_1) - \int dx_1 dx'_1 \hat{\psi}^\dagger(x'_1) v^{\text{HF}}(x'_1, x_1) \hat{\psi}(x_1) \right]. \end{aligned} \quad (2.1)$$

The circumflex indicates second quantized operators and  $\lambda$  is an order parameter ranging from 0 to 1. For  $\lambda = 1$  the above Hamiltonian is equal to the full many electron Hamiltonian and for  $\lambda = 0$  it is equal to the Fock operator that will serve as the zero order and which can be obtained in diagonal form

$$\hat{F} = \hat{H}(0) = \sum_i \epsilon_i \hat{a}_i^\dagger \hat{a}_i. \quad (2.2)$$

The operators  $\hat{a}_i^\dagger$  and  $\hat{a}_i$  are the creation and destruction operators, respectively, for a Hartree–Fock particle. The wave function as well as the energy that correspond to  $\hat{H}(\lambda)$  become  $\lambda$  dependent according to the Schrödinger equation

$$\hat{H}(\lambda)|\Psi(\lambda)\rangle = E(\lambda)|\Psi(\lambda)\rangle \quad (2.3)$$

and as a result the single-particle propagator<sup>12</sup> becomes  $\lambda$  dependent:

$$G(1,1',\lambda) = \frac{1}{i} \langle \Psi_H(\lambda) | T \hat{\psi}_H(1,\lambda) \hat{\psi}_H^\dagger(1',\lambda) | \Psi_H(\lambda) \rangle. \quad (2.4)$$

$$E(\lambda) = \langle \Psi(\lambda) | \hat{h} + \hat{v}^{\text{HF}} + \lambda(\hat{V} - \hat{v}^{\text{HF}}) | \Psi(\lambda) \rangle \quad (2.8)$$

$$= \langle \Psi(\lambda) | \hat{h} + \hat{v}^{\text{HF}} | \Psi(\lambda) \rangle + \lambda \langle \Psi(\lambda) | \hat{V} - \hat{v}^{\text{HF}} | \Psi(\lambda) \rangle \quad (2.9)$$

$$= \int dx_1 dx_1' [h(x_1)\delta(x_1 - x_1') + v^{\text{HF}}(x_1, x_1')] \rho(x_1', x_1, \lambda) + \lambda \langle \Psi(\lambda) | \hat{V} - \hat{v}^{\text{HF}} | \Psi(\lambda) \rangle. \quad (2.10)$$

While the term involving the density can be obtained from Eq. (2.6), the second term can be obtained from the time derivative of  $G(1,1',\lambda)$  with respect to  $t_1$ ,

$$i \frac{\partial}{\partial t_1} G(1,1',\lambda) = \langle \Psi_H(\lambda) | T \frac{\partial}{\partial t_1} \hat{\psi}_H(1,\lambda) \hat{\psi}_H^\dagger(1',\lambda) | \Psi_H(\lambda) \rangle + \delta(x_1 - x_1') \delta(t_1 - t_1') \quad (2.11)$$

$$= \frac{1}{i} \langle \Psi_H(\lambda) | T [ \hat{\psi}_H(1,\lambda), \hat{H} ] - \hat{\psi}_H^\dagger(1',\lambda) | \Psi_H(\lambda) \rangle + \delta(x_1 - x_1') \delta(t_1 - t_1'). \quad (2.12)$$

The  $\delta$  functions emerge as a consequence of differentiating the  $\theta$  function which in turn arises from the time ordering operator. When we later take the limit  $t_1 - t_1' \rightarrow 0^-$  there will be no contribution from this  $\delta$  function. The commutator in Eq. (2.12) can now be evaluated

$$[\hat{\psi}_H(1,\lambda), \hat{H}]_- = e^{i\hat{H}(\lambda)t_1} [ \hat{\psi}(x_1), \hat{h} + \hat{v}^{\text{HF}} ]_- e^{-i\hat{H}(\lambda)t_1} + \lambda e^{i\hat{H}(\lambda)t_1} [ \hat{\psi}(x_1), \hat{V} - \hat{v}^{\text{HF}} ]_- e^{-i\hat{H}(\lambda)t_1}. \quad (2.13)$$

Since the commutators in Eq. (2.13) are  $\lambda$  independent they can immediately be evaluated in the usual way.<sup>1</sup> In the limit of equal times we have

$$\begin{aligned} & \frac{1}{i} \lim_{t_1 - t_1' \rightarrow 0^-} i \frac{\partial}{\partial t_1} G(1,1',\lambda) \\ &= \int dx_2 [ h(x_1)\delta(x_1 - x_2) + v^{\text{HF}}(x_1, x_2) ] \rho(x_2, x_1') \\ &+ \lambda \int dx_2 [ V(x_1, x_2) \rho(x_1, x_2, x_1', x_2) \\ &- v^{\text{HF}}(x_1, x_2) \rho(x_2, x_1') ], \end{aligned} \quad (2.14)$$

The symbol  $T$  stands for the Wick time-ordering operator and the subscript  $H$  refers to the ( $\lambda$  dependent) Heisenberg picture

$$\hat{\psi}_H^\dagger(1,\lambda) = \hat{\psi}_H^\dagger(x_1, t_1, \lambda) = e^{i\hat{H}(\lambda)t_1} \hat{\psi}^\dagger(x_1) e^{-i\hat{H}(\lambda)t_1}. \quad (2.5)$$

Just as in the case of the full Hamiltonian ( $\lambda = 1$ ) we obtain the density which, however, is now  $\lambda$  dependent, in the limit where  $t_1$  approaches  $t_1'$ :

$$\begin{aligned} \frac{1}{i} \lim_{t_1 - t_1' \rightarrow 0^-} G(1,1',\lambda) &= \langle \Psi(\lambda) | \hat{\psi}^\dagger(x_1') \hat{\psi}(x_1) | \Psi(\lambda) \rangle \\ &= \rho(x_1, x_1', \lambda). \end{aligned} \quad (2.6)$$

The wave function and the field operators in equation (2.6) have been transformed back to the Schrödinger picture.

We now wish to express the total energy  $E(\lambda)$  in terms of the Green's function (2.4). We use the following shorthand notation for the Hamiltonian (2.1)

$$\hat{H} = \hat{h} + \hat{v}^{\text{HF}} + \lambda(\hat{V} - \hat{v}^{\text{HF}}), \quad (2.7)$$

where the four terms in Eq. (2.7) stand for the four terms in Eq. (2.1), respectively. The total energy now reads

where  $\rho(x_1, x_1', x_2, x_2')$  is the two-electron density matrix. Using Eqs. (2.6), (2.10), and (2.14) the total energy can be written as

$$\begin{aligned} E(\lambda) &= \frac{1}{2} \int dx_1 \lim_{x_1' \rightarrow x_1} \frac{1}{i} \lim_{t_1 - t_1' \rightarrow 0^-} \left[ i \frac{\partial}{\partial t_1} + h(x_1) \right. \\ &\quad \left. + v^{\text{HF}}(x_1', x_1) - \lambda v^{\text{HF}}(x_1', x_1) \right] G(1,1',\lambda). \end{aligned} \quad (2.15)$$

This follows after making the observation that the total electron–electron repulsion energy  $\langle \hat{V} \rangle$  is obtained twice from the trace of Eq. (2.14). All other terms in Eq. (2.14) are therefore added once more and the result is divided by 2 to arrive at Eq. (2.15). Now that we have a general expression for the total energy in terms of the order parameter  $\lambda$  it is possible to identify contributions to the total energy order by order. It is then most convenient to Fourier transform obtaining

$$E(\lambda) = \frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega (\omega + F - \lambda v^{\text{HF}}) G(\omega, \lambda) \quad (2.16)$$

in which  $F$ ,  $v^{\text{HF}}$ , and  $G(\omega, \lambda)$  are the matrix equivalents of the corresponding quantities in Eq. (2.15). The time limit now corresponds to a contour integral and the time derivative yields a multiplicative factor  $\omega$ . The contour should enclose all the ionization poles of  $G(\omega, \lambda)$ . For  $\lambda = 1$ , Eq. (2.16) reduces to the familiar energy expression<sup>12</sup>

$$E = \frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega (\omega + h) G(\omega). \quad (2.17)$$

Note, however, that this expression is not correct for intermediate values of  $\lambda$ .

To make further progress we expand the total energy and the Green's function in orders of  $\lambda$ :

$$E(\lambda) = \sum_{n=0}^{\infty} \lambda^n E^{(n)}, \quad (2.18)$$

$$G(\omega, \lambda) = \sum_{n=0}^{\infty} \lambda^n G^{(n)}(\omega), \quad (2.19)$$

where  $E^{(n)}$  and  $G^{(n)}(\omega)$  are the  $n$ th order contributions to  $E(\lambda)$  and  $G(\omega, \lambda)$ . Substituting Eqs. (2.18) and (2.19) in Eq. (2.16) we can identify the  $n$ th order contribution to the total energy as

$$E^{(n)} = \frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega (\omega + F) G^{(n)}(\omega) - \frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega v^{\text{HF}} G^{(n-1)}(\omega). \quad (2.20)$$

Formula (2.20) establishes the relation between the total energy and the Green's function order by order. Note that for the  $n$ th order energy the  $n$ th as well as the  $(n-1)$ th order Green's function is needed. For  $n = 2$  a similar analysis has been performed by Jaszuński, Pickup, and McWeeny.<sup>13</sup>

The lowest order contributions can be easily obtained from Eq. (2.20) and it can thus be seen how they reduce to the well known expressions from the Møller–Plesset perturbation theory.<sup>2</sup> For the zero order energy we only need  $G^{(0)}(\omega)$  which reads in the basis of the Hartree–Fock orbitals<sup>12</sup>

$$G_{pq}^{(0)}(\omega) = \frac{\delta_{pq} n_p}{\omega - \epsilon_p - i\eta} + \frac{\delta_{pq} \bar{n}_p}{\omega - \epsilon_p + i\eta}. \quad (2.21)$$

Here  $\bar{n}_p = (1 - n_p)$  with  $n_p$  the occupation number of orbital  $p$  (0 or 1),  $\eta$  a positive infinitesimal convergence factor, and  $\epsilon_p$  from Eq. (2.2). It now immediately follows that

$$E^{(0)} = \frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega (\omega + \epsilon) G^{(0)}(\omega) = \sum_i n_i \epsilon_i, \quad (2.22)$$

i.e., the zero order energy is just the sum of the occupied orbital energies. Successive contributions  $G^{(n)}(\omega)$  can be obtained by iterating the Dyson equation

$$G = G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \dots \quad (2.23)$$

and expanding the self-energy order by order as is done for  $G(\omega)$  in Eq. (2.19). The lowest contribution to  $\Sigma(\omega)$  is of second order, therefore  $G^{(1)}(\omega) = 0$ . This means that

$$E^{(1)} = -\frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega v^{\text{HF}} G^{(0)}(\omega) = -\frac{1}{2} \sum_i v_{ii}^{\text{HF}} n_i. \quad (2.24)$$

On summing Eqs. (2.22) and (2.24) we obtain the Hartree–Fock energy

$$E^{\text{HF}} = E^{(0)} + E^{(1)} = \frac{1}{2} \sum_i (h_{ii} + \epsilon_i) n_i. \quad (2.25)$$

Now one is able to understand why the general energy formula (2.17) when applied to the zero order Green's function already produces the zero plus the first order energy

$$\frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega (\omega + h) G^{(0)}(\omega) = \frac{1}{2} \sum_i (h_{ii} + \epsilon_i) n_i. \quad (2.26)$$

The reason is that the one-electron term  $h$  in Eq. (2.26) is not of zero order, but the Fock operator is [cf. (2.22)]. Of more interest of course are the second and higher order contributions. From Eq. (2.20) it follows that

$$E^{(2)}(\omega) = \frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega (\omega + F) G^{(2)}(\omega), \quad (2.27)$$

where

$$G^{(2)}(\omega) = G^{(0)}(\omega) \Sigma^{(2)}(\omega) G^{(0)}(\omega). \quad (2.28)$$

$G^{(2)}(\omega)$  is not simply related to what is known as the second order Green's function which we will denote as  $G^{\text{Dyson}(2)}(\omega)$  since it is obtained by solving the Dyson equation<sup>11</sup>

$$G^{\text{Dyson}(2)}(\omega) = [G^{(0)-1}(\omega) - \Sigma^{(2)}(\omega)]^{-1} - G^{(0)}(\omega) \quad (2.29)$$

which is equivalent to iterating formula (2.23) to infinite order using  $\Sigma^{(2)}(\omega)$ .

It is interesting to see how Eq. (2.27) reduces to the well known MP(2) approximation for the correlation energy. We then need the expression for the second order self-energy<sup>5</sup>

$$\Sigma_{pq}^{(2)}(\omega) = \frac{1}{2} \sum_{ab} \frac{\langle pi || ab \rangle \langle ab || qi \rangle}{\omega - \epsilon_a - \epsilon_b + \epsilon_i + i\eta} + \frac{1}{2} \sum_{ij} \frac{\langle pa || ij \rangle \langle ij || qa \rangle}{\omega - \epsilon_i - \epsilon_j + \epsilon_a - i\eta}. \quad (2.30)$$

Here we have adopted the convention that  $a, b, \dots$  stand for unoccupied orbitals whereas  $i, j, \dots$  stand for occupied orbitals and  $p, q, \dots$  for general (occupied or unoccupied) orbitals. Substitution of  $G^{(2)}(\omega)$  in Eq. (2.27) by means of Eq. (2.28) yields

$$E^{(2)} = \frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega \Sigma^{(2)}(\omega) G^{(0)}(\omega) + \text{Tr} \epsilon \frac{1}{2\pi i} \oint d\omega G^{(0)}(\omega) \Sigma^{(2)}(\omega) G^{(0)}(\omega), \quad (2.31)$$

where we used the fact that

$$\omega G^{(0)}(\omega) = 1 + \epsilon G^{(0)}(\omega). \quad (2.32)$$

Evaluating the first term in Eq. (2.31) yields

$$\frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega \Sigma^{(2)}(\omega) G^{(0)}(\omega)$$

$$= \frac{1}{2} \sum_{ab} \frac{\langle ab || ij \rangle \langle ij || ab \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b} \quad (2.33)$$

which is twice the MP(2) result. The second term yields

$$\begin{aligned} \text{Tr} \epsilon \frac{1}{2\pi i} \oint d\omega G^{(0)}(\omega) \Sigma^{(2)}(\omega) G^{(0)}(\omega) \\ = -\frac{1}{4} \sum_{ab} \frac{\langle ij || ab \rangle \langle ab || ij \rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \end{aligned} \quad (2.34)$$

By adding Eqs. (2.33) and (2.34) we recover the usual MP(2) result

$$E^{(2)} = \frac{1}{4} \sum_{ab} \frac{||\langle ij || ab \rangle||^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}. \quad (2.35)$$

To analyze the difference in energy as obtained from the MP(2) method, as opposed to the second order Green's function method, cf. Eq. (2.29), we define the correction to the Hartree–Fock energy as

$$E^{\text{Dyson}(2)} = \frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega (\omega + h) G^{\text{Dyson}(2)}(\omega). \quad (2.36)$$

The MP(2) energy on the other hand is obtained from Eq. (2.27) which can be written in the form

$$\begin{aligned} E^{(2)} = \frac{1}{2} \text{Tr} \frac{1}{2\pi i} \oint d\omega (\omega + h) G^{(2)}(\omega) \\ + \frac{1}{2} \text{Tr} v^{\text{HF}}(\rho^{\text{HF}})\rho^{(2)}. \end{aligned} \quad (2.37)$$

Comparing Eqs. (2.36) and (2.37) there are two differences. First, Eq. (2.37) contains  $G^{(2)}$  instead of  $G^{\text{Dyson}(2)}$ . This reflects the summation of terms up to infinite order in the interaction

$$G^{\text{Dyson}(2)} = G^{(0)}\Sigma^{(2)}G^{(0)} + G^{(0)}\Sigma^{(2)}G^{(0)}\Sigma^{(2)}G^{(0)} + \dots, \quad (2.38)$$

whereas  $G^{(2)}$  is made up of the first term at the rhs of Eq. (2.38), cf. Eq. (2.28). This difference affects the one-electron contributions as well as the two-electron contributions to the total energy. Second, Eq. (2.37) has the additional term  $\frac{1}{2} \text{Tr} v^{\text{HF}}(\rho^{\text{HF}})\rho^{(2)}$  which only affects the two-electron contribution to the total energy.

Formulas (2.36) and (2.37) can be expressed in terms of the contributions  $\Gamma^1$  and  $\Gamma^{\text{corr}}$  to the electron repulsion energy density  $\Gamma$  defined in a previous paper by the authors which is referred to as I.<sup>14</sup>  $\Gamma^1$  and  $\Gamma^{\text{corr}}$  read

$$\Gamma^1(x_1, x_1') = \int dx_2 v^{\text{HF}}(x_1, x_2, \rho^{\text{HF}}) \Delta\rho(x_2, x_1') \quad (2.39)$$

and

$$\Gamma^{\text{corr}}(x_1, x_1') = \frac{1}{i} \lim_{t, -t; -t, -t} \int d2 \Sigma'(1, 2) G(2, 1') \quad (2.40)$$

in terms of which expressions (2.36) and (2.37) read

$$E^{(2)} = \text{Tr} h\rho^{(2)} + \text{Tr} \Gamma^{(2)} + \frac{1}{2} \text{Tr} \Gamma^{\text{corr}(2)} \quad (2.41)$$

and

$$E^{\text{Dyson}(2)} = \text{Tr} h\rho^{\text{Dyson}(2)} + \frac{1}{2} \text{Tr} \Gamma^{\text{Dyson}(2)} + \frac{1}{2} \text{Tr} \Gamma^{\text{corr} \text{Dyson}(2)}, \quad (2.42)$$

respectively. The superscripts (2) and Dyson(2) in formulas (2.41) and (2.42) are added to indicate that the superscript quantities result from the true second order term  $G^{(2)}(\omega)$  in expansion (2.19) and from  $G^{\text{Dyson}(2)}(\omega)$  defined in Eq. (2.29), respectively.

Apart from the absence of higher than second order terms in the Green's function the MP(2) energy has a factor 1 in front of  $\Gamma^{(2)}$  instead of a factor  $\frac{1}{2}$  in  $E^{\text{Dyson}(2)}$ . It is therefore of interest to determine whether it is the infinite summation or the absence of the last term at the rhs of Eq. (2.37) in (2.36) that accounts for the difference between the second order Green's function energy and the MP(2) energy.

It is worthwhile to note another difference between  $G^{(2)}(\omega)$  and  $G^{\text{Dyson}(2)}(\omega)$ . The trace of the density obtained from an approximate Green's function does not in general conserve the number of electrons. This is due to the fact that, for example,  $G^{\text{Dyson}(2)}(\omega)$  is not consistent in orders, it contains fourth, sixth, and higher order terms but not all fourth, sixth, and higher order terms. If however the density is calculated in a way consistent through the  $n$ th order the number of electrons is conserved since from Eq. (2.19) one deduces

$$\text{Tr} \rho^{(0)} = N \text{ and } \text{Tr} \rho^{(n)} = 0, \quad n = 1, 2, \dots \quad (2.43)$$

For the second order this can be explicitly verified as follows

$$\begin{aligned} \text{Tr} \rho^{(2)} &= \text{Tr} \frac{1}{2\pi i} \oint d\omega G^{(2)}(\omega) \\ &= \text{Tr} \frac{1}{2\pi i} \oint d\omega G^{(0)}(\omega) \Sigma^{(2)}(\omega) G^{(0)}(\omega). \end{aligned} \quad (2.44)$$

Evaluating the contour integral we obtain

$$\begin{aligned} \text{Tr} \frac{1}{2\pi i} \oint d\omega G^{(0)}(\omega) \Sigma^{(2)}(\omega) G^{(0)}(\omega) \\ = -\frac{1}{2} \sum_{ab} \frac{\langle ji || ab \rangle \langle ab || ji \rangle}{(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)^2} \\ + \frac{1}{2} \sum_{ab} \frac{\langle ji || ab \rangle \langle ab || ji \rangle}{(\epsilon_a + \epsilon_b - \epsilon_i - \epsilon_j)^2} \\ = 0. \end{aligned} \quad (2.45)$$

### III. ANALYSIS FOR H<sub>2</sub> IN A MINIMAL BASIS

As an illustration of the considerations in Sec. II we will apply the formalism to the H<sub>2</sub> molecule in a minimal basis. This approach has the advantage that the problem can be treated analytically rather than numerically. Moreover this very simple system is capable of illustrating various aspects of the Green's function approach by varying the internuclear distance  $R$ . At small internuclear distances the Hartree–Fock method provides an accurate solution and consequently serves as a good zero order starting point for both the MP(2) and GF(2) perturbative corrections. At large inter-

nuclear distances the Hartree–Fock zero order solution is much less accurate. Furthermore traditional Møller–Plesset perturbation theory completely breaks down due to the degeneracy of the Hartree–Fock eigenvalues. It will be shown that the Green's function approach does not suffer from this drawback. The second order Green's function provides accurate results at large internuclear distances and even generates the exact solution in the limit  $R \rightarrow \infty$  provided the system is described in the minimal basis of atomic hydrogen functions. As a consequence there is an interval of intermediate distances where the deviation from the exact solution is largest, reaching a maximum of about  $5a_0$ .

The minimal basis  $H_2$  problem is treated in many textbooks<sup>15</sup> and is in fact a one-parameter model in the internuclear distance  $R$ . Not all quantities can be simply expressed in terms of  $R$  though, except in the limit  $R \rightarrow \infty$ . The exact Green's function can be obtained from the Lehmann representation<sup>12</sup>

$$G_{ij}(\omega) = \sum_m \frac{g_i^m g_j^{m*}}{\omega - \beta_m - i\eta} + \sum_n \frac{f_i^n f_j^{n*}}{\omega - \alpha_n + i\eta} \quad (3.1)$$

in which the Feynman–Dyson amplitudes are defined as<sup>1</sup>

$$g_i^m = \langle \Psi^m(N-1) | \hat{a}_i | \Psi(N) \rangle \quad (3.2)$$

and

$$f_i^n = \langle \Psi(N) | \hat{a}_i | \Psi^n(N+1) \rangle \quad (3.3)$$

and  $\beta$  and  $\alpha$  correspond to the negatives of the ionization potentials and electron attachment energies, respectively,

$$\beta_m = E(N) - E^m(N-1) \quad (3.4)$$

and

$$\alpha_n = E^n(N+1) - E(N). \quad (3.5)$$

Here  $\Psi^m(N-1)$  denotes a  $N-1$  electron state and  $\Psi^n(N+1)$  denotes a  $N+1$  electron state. In the case under consideration we have  $N=2$ . To calculate the Feynman–Dyson amplitudes we thus need the two-electron ground state and the one- and three-electron states. The matrix  $G_{ij}(\omega)$  blocks into two identical blocks due to spin symmetry. Therefore  $i$  and  $j$  can be restricted to be of spin-up type, say, and  $G_{ij}(\omega)$  is a  $2 \times 2$  matrix. The Hartree–Fock orbitals are determined by symmetry and read

$$g(x) = \frac{1}{\sqrt{2(1+S)}} (A(x) + B(x)) \quad (3.6)$$

and

$$u(x) = \frac{1}{\sqrt{2(1-S)}} (A(x) - B(x)), \quad (3.7)$$

where  $S$  is the overlap between the basis functions  $A(x)$  and  $B(x)$  which are the atomic hydrogen  $1s$  functions centered on the nuclei labeled  $A$  and  $B$  and separated by a distance  $R$ . The gerade and ungerade orbitals (3.6) and (3.7) will be numbered 1 and 2, respectively. The normalized Hartree–Fock solution of the ground state reads<sup>15</sup>

$$|\Psi_{\text{HF}}\rangle = |\bar{1}\bar{1}\rangle \quad (3.8)$$

and the normalized exact solution reads<sup>15</sup>

$$|\Psi(N)\rangle = \frac{1}{\sqrt{1+c^2}} [|\bar{1}\bar{1}\rangle + c|2\bar{2}\rangle], \quad (3.9)$$

where the coefficient  $c$  has to be determined from the CI matrix. The Hartree–Fock orbitals are the only orbitals that can be constructed in this model and are therefore also the exact one-electron states. From the states  $|1\rangle$ ,  $|\bar{1}\rangle$ ,  $|2\rangle$ , and  $|\bar{2}\rangle$  one can construct eight  $g_i^m$  type amplitudes, two of which contribute to  $G_{ij}(\omega)$ :

$$g_1^1 = \langle \bar{1} | \hat{a}_1 | \Psi(N) \rangle = \frac{1}{\sqrt{1+c^2}}, \quad (3.10)$$

$$g_2^2 = \langle \bar{2} | \hat{a}_2 | \Psi(N) \rangle = \frac{c}{\sqrt{1+c^2}}. \quad (3.11)$$

In the same way the contributing  $f_i^n$  amplitudes can be constructed from the three-electron states  $|1\bar{1}\bar{2}\rangle$ ,  $|\bar{1}\bar{1}\bar{2}\rangle$ ,  $|12\bar{2}\rangle$ , and  $|\bar{1}\bar{2}\bar{2}\rangle$  yielding

$$f_1^1 = \langle \Psi(N) | \hat{a}_1 | 2\bar{2}\bar{1} \rangle = \frac{c}{\sqrt{1+c^2}}, \quad (3.12)$$

$$f_2^2 = \langle \Psi(N) | \hat{a}_2 | 1\bar{1}\bar{2} \rangle = \frac{1}{\sqrt{1+c^2}}. \quad (3.13)$$

The Green's function can now be written down as

$$G(\omega) = \frac{1}{1+c^2} \begin{pmatrix} \frac{1}{\omega - \beta_1} + \frac{c^2}{\omega - \alpha_1} & 0 \\ 0 & \frac{c^2}{\omega - \beta_2} + \frac{1}{\omega - \alpha_2} \end{pmatrix}. \quad (3.14)$$

The quantities  $c$ ,  $\beta_1$ ,  $\beta_2$ ,  $\alpha_1$ , and  $\alpha_2$  can all be expressed in terms of one- and two-electron integrals as follows. Let  $E^{\text{HF}}$  be the Hartree–Fock energy and  $E^c$  the correlation energy [i.e.,  $E(N) = E^{\text{HF}} + E^c$ ],  $\epsilon_1$  and  $\epsilon_2$  the eigenvalues of the Fock operator. We then have the one-electron integrals  $h_{11}$  and  $h_{22}$ , the Coulomb integrals  $\langle 1|11 \rangle = J_{11}$ ,  $\langle 12|12 \rangle = J_{12}$ ,  $\langle 22|22 \rangle = J_{22}$  and the exchange integral  $\langle 1|22 \rangle = K_{12}$ . From Eqs. (3.4) and (3.5) now follow

$$\begin{aligned} \beta_1 &= E^{\text{HF}} + E^c - h_{11} \\ &= 2h_{11} + J_{11} + E^c - h_{11} = \epsilon_1 + E^c, \end{aligned} \quad (3.15)$$

$$\begin{aligned} \beta_2 &= E^{\text{HF}} + E^c - h_{22} \\ &= 2\epsilon_1 - \epsilon_2 - J_{11} + 2J_{12} - K_{12} + E^c, \end{aligned} \quad (3.16)$$

$$\begin{aligned} \alpha_1 &= \langle 2\bar{2}\bar{1} | \hat{H} | 2\bar{2}\bar{1} \rangle - E(N) \\ &= 2\epsilon_2 - \epsilon_1 + J_{22} - 2J_{12} + K_{12} - E^c, \end{aligned} \quad (3.17)$$

$$\begin{aligned} \alpha_2 &= \langle 1\bar{1}\bar{2} | \hat{H} | 1\bar{1}\bar{2} \rangle - E(N) \\ &= \epsilon_2 - E^c, \end{aligned} \quad (3.18)$$

whereas<sup>15</sup>

$$E^c = \Delta - \sqrt{\Delta^2 + K_{12}^2}, \quad (3.19)$$

$$\Delta = \epsilon_2 - \epsilon_1 + \frac{1}{2}(J_{11} + J_{22} - 2J_{12} + K_{12}), \quad (3.20)$$

$$c = \frac{E^c}{K_{12}} = \frac{K_{12}}{E^c - 2\Delta}. \quad (3.21)$$

In order to obtain the exact self-energy expression (3.14) can be manipulated algebraically to yield

$$G^{-1}(\omega) = \omega 1 - \begin{bmatrix} \frac{\beta_1 + \alpha_1 c^2}{1 + c^2} + \left\{ \frac{c^2(\alpha_1 - \beta_1)^2}{(1 + c^2)^2} \right\} / \left[ \omega - \left( \frac{\alpha_1 + \beta_1 c^2}{1 + c^2} \right) \right] \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ \frac{\beta_2 c^2 + \alpha_2}{1 + c^2} + \left\{ \frac{c^2(\alpha_2 - \beta_2)^2}{(1 + c^2)^2} \right\} / \left[ \omega - \left( \frac{\alpha_2 c^2 + \beta_2}{1 + c^2} \right) \right] \end{bmatrix} \quad (3.22)$$

If we partition the self-energy into an energy-dependent part  $\Sigma'(\omega)$  and an energy-independent part  $\Sigma(\infty)$ ,<sup>16</sup> the Dyson equation reads

$$G^{-1}(\omega) = [\omega 1 - \epsilon - \Sigma(\infty) - \Sigma'(\omega)] \quad (3.23)$$

and we can immediately identify

$$\Sigma'(\omega) = \frac{c^2}{(1 + c^2)^2} \begin{bmatrix} (\alpha_1 - \beta_1)^2 / \left( \omega - \frac{\alpha_1 + \beta_1 c^2}{1 + c^2} \right) \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ (\alpha_2 - \beta_2)^2 / \left( \omega - \frac{\alpha_2 c^2 + \beta_2}{1 + c^2} \right) \end{bmatrix}. \quad (3.24)$$

Notice that  $\Sigma'(\omega)$  like  $G^{\text{HF}}(\omega)$  has only one singularity in each symmetry, while the full Green's function (3.22) has two singularities in each symmetry corresponding to an ionization energy and an electron attachment energy.

We will now determine the behavior of  $\Sigma'(\omega)$  at large internuclear distances which follows from the behavior of the molecular one- and two-electron integrals whose behavior in turn follows from the atomic integrals. Retaining only terms linear in  $1/R$  we have

$$\langle A | \hat{h} | A \rangle = h - \frac{1}{R} + O\left(\frac{1}{R^2}\right), \quad (3.25a)$$

$$\langle 1 | \hat{h} | 1 \rangle = h - \frac{1}{R} + O\left(\frac{1}{R^2}\right), \quad (3.25b)$$

$$\langle 2 | \hat{h} | 2 \rangle = h - \frac{1}{R} + O\left(\frac{1}{R^2}\right), \quad (3.25c)$$

$$\langle AA | AA \rangle = J + O\left(\frac{1}{R^2}\right), \quad (3.25d)$$

$$\langle AB | AB \rangle = \frac{1}{R} + O\left(\frac{1}{R^2}\right), \quad (3.25e)$$

$$\langle AA | BB \rangle = O\left(\frac{1}{R^2}\right). \quad (3.25f)$$

Here (3.25a) and (3.25d) define  $h$  and  $J$ , respectively. The integral  $\langle AA | BB \rangle$  decays faster than  $1/R$ . For the molecular integrals we thus find

$$J_{11}, J_{12}, J_{22} = \frac{1}{2} \left( J + \frac{1}{R} \right) + O\left(\frac{1}{R^2}\right), \quad (3.25g)$$

$$K_{12} = \frac{1}{2} \left( J - \frac{1}{R} \right) + O\left(\frac{1}{R^2}\right), \quad (3.25h)$$

and finally

$$\beta_1, \beta_2 = h + O\left(\frac{1}{R^2}\right), \quad (3.25i)$$

$$\alpha_1, \alpha_2 = h + J + O\left(\frac{1}{R^2}\right), \quad (3.25j)$$

$$c = -1 + O\left(\frac{1}{R^2}\right), \quad (3.25k)$$

$$\Delta = O\left(\frac{1}{R^2}\right), \quad (3.25l)$$

$$\epsilon_1 = h + \frac{1}{2} \left( J - \frac{1}{R} \right) + O\left(\frac{1}{R^2}\right), \quad (3.25m)$$

$$\epsilon_2 = h + \frac{1}{2} \left( J + \frac{1}{R} \right) + O\left(\frac{1}{R^2}\right). \quad (3.25n)$$

The behavior of  $\Sigma'(\omega)$  in the limit of large  $R$  can now be determined from (3.24) and (3.25) which yields

$$\Sigma'(\omega) = \begin{bmatrix} \frac{J^2}{4} / \left[ \omega - \left( h + \frac{J}{2} \right) \right] \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ \frac{J^2}{4} / \left[ \omega - \left( h + \frac{J}{2} \right) \right] \end{bmatrix} + O\left(\frac{1}{R^2}\right). \quad (3.26)$$

The expression for the *second order* self-energy in the same limit can be obtained from Eqs. (2.30) and (3.25) and reads

$$\Sigma'^{(2)}(\omega) = \begin{bmatrix} \left( \frac{J^2}{4} - \frac{J}{2R} \right) / \left[ \omega - \left( h + \frac{J}{2} + \frac{5}{2R} \right) \right] \\ 0 \end{bmatrix} \begin{bmatrix} 0 \\ \left( \frac{J^2}{4} - \frac{J}{2R} \right) / \left[ \omega - \left( h + \frac{J}{2} - \frac{1}{2R} \right) \right] \end{bmatrix} + O\left(\frac{1}{R^2}\right). \quad (3.27)$$

Surprisingly expressions (3.26) and (3.27) differ only in the coefficients of the  $1/R$  term which means that the dynamic second order self-energy becomes exact in the limit of  $R \rightarrow \infty$ . Furthermore it follows from (3.22), (3.23), and (3.25) that

$$(\epsilon + \Sigma(\infty)) = \begin{bmatrix} h + \frac{J}{2} & 0 \\ 0 & h + \frac{J}{2} \end{bmatrix} + O\left(\frac{1}{R^2}\right), \quad (3.28)$$

whereas in the second order approximations for the self-energy the energy independent part is zero and we thus have  $(\epsilon + \Sigma(\infty))^{(2)}$

$$= \begin{bmatrix} h + \frac{J}{2} - \frac{1}{2R} & 0 \\ 0 & h + \frac{J}{2} + \frac{1}{2R} \end{bmatrix} + O\left(\frac{1}{R^2}\right), \quad (3.29)$$

which again only differs from (3.28) in the coefficients of the

$1/R$  term. It now has been proven that the second order Green's function for the minimal basis  $H_2$  system becomes exact at infinite internuclear distance.

This means that the Green's function obtained from the second order self-energy is identical to the Green's function obtained from the full CI wave function. Moreover, since the minimal basis is made up of the atomic hydrogen  $s$  functions, the energy obtained from Green's function (3.14) becomes exact for the  $H_2$  system at infinite internuclear distance. As a consequence we have in this case

$$\lim_{R \rightarrow \infty} [E^{\text{Dyson}(2)} + E^{\text{HF}}] = -1.0E_h. \quad (3.30)$$

If on the other hand the MP(2) energy is calculated, one obtains from Eq. (2.40)

$$\begin{aligned} \lim_{R \rightarrow \infty} [E^{\text{HF}} + E^{(2)}] &= \lim_{R \rightarrow \infty} \left[ 2\epsilon_1 - J_{11} + \frac{1}{2} \frac{\langle 11|22 \rangle^2}{\epsilon_1 - \epsilon_2} \right] \\ &= \lim_{R \rightarrow \infty} \left[ 2h + J - \frac{R}{2} K_{12}^2 \right] \\ &= -\infty. \end{aligned} \quad (3.31)$$

The striking difference between Eqs. (3.30) and (3.31) is due to the fact that  $E^{(2)}$  is calculated from Eq. (2.27) which contains only the second order term  $G^{(2)}(\omega)$  whereas  $E^{\text{Dyson}(2)}$  is calculated from Eq. (2.41) which contains some contributions  $G^{(n)}(\omega)$  up to infinite order. The effect of keeping all terms up to infinite order can also be seen as follows. Consider the limit  $R \rightarrow \infty$  and suppose one aims to calculate  $G_{11}^{(2)}(\omega)$  by explicitly summing the Dyson series (2.23)

$$\begin{aligned} G_{11}(\omega) &= G_{11}^{(0)}(\omega) \sum_{k=0}^{\infty} [\Sigma_{11}(\omega) G_{11}^{(0)}(\omega)]^k \\ &= \frac{1}{\omega - \epsilon} \sum_{k=0}^{\infty} \left[ \frac{J^2}{4(\omega - \epsilon)^2} \right]^k. \end{aligned} \quad (3.32)$$

If the summation in Eq. (3.32) is cut off at some finite value  $k$  the resulting Green's function always has a singularity at  $\omega = \epsilon$ . If, however, the whole series is summed one obtains [cf. Eq. (3.14)]

$$\begin{aligned} G_{11}(\omega) &= \frac{1}{\omega - \epsilon} \left[ 1 / \left( 1 - \frac{J^2}{4(\omega - \epsilon)^2} \right) \right] \\ &= \left[ (\omega - \epsilon) / \left( \omega - \epsilon + \frac{J}{2} \right) \left( \omega - \epsilon - \frac{J}{2} \right) \right] \\ &= \frac{1}{2} \left( \frac{1}{\left[ \omega - \left( \epsilon - \frac{J}{2} \right) \right]} + \frac{1}{\left[ \omega - \left( \epsilon + \frac{J}{2} \right) \right]} \right), \end{aligned} \quad (3.33)$$

i.e., a Green's function with two simple poles that are shifted an amount  $\pm J/2$ , respectively, with respect to the original pole at  $\omega = \epsilon$ . The density matrix element corresponding to Eq. (3.33) is  $\rho_{11} = \frac{1}{2}$ . If one on the other hand calculates  $\rho_{11}^{(2)}$  one obtains, see Eqs. (2.47) and (2.48)

$$\rho_{11}^{(2)} = - \left( \frac{J}{2} \right)^2 / 4(\epsilon_2 - \epsilon_1)^2 = -\infty. \quad (3.34)$$

## IV. RESULTS

In this section we discuss the results of calculations performed on a number of small systems. In subsection A attention will be focused upon the He and Be atoms and the LiH molecule. In subsection B the hydrogen molecule is studied, now in a large basis set. Finally, in subsection C the iso-electronic series Ne, HF,  $H_2O$ ,  $NH_3$ ,  $CH_4$  is studied. It turns out that the effect of correlating the motion of the electrons on the systems Ne, HF,  $H_2O$  is different from the general trend: the density expands slightly instead of contracting. This effect has important consequences in the interpretation of the results.

### A. He, Be, LiH

The basis sets as well as the type of CI calculation for He, Be, and LiH were the same as those used in I. The basis set and geometry used for LiH is referred to as 'basis 3' in I, consisting of 44 functions in total whereas the He and Be bases both comprise 32 functions.

The results for these systems are collected in Tables I–III. Considering the He atom first (Table I) it is clear that the total electronic energy  $E^{\text{el}}$  produced by the second order Green's function method (GF(2)) is closer to the full CI result than the sum of the Hartree–Fock and the Møller–Plesset result (MP(2)). Considering the two terms  $h$  and  $V_{ee}$  that together constitute  $E^{\text{el}}$  it is also clear that the difference between the MP(2) and GF(2) total energy  $E^{\text{el}}$  is fully attributable to the difference in the  $V_{ee}$  contribution. Since the one-electron contribution  $h$  differs only in the fourth decimal for MP(2) and GF(2) it is strongly suggested that the density obtained from the GF(2) method is almost identical to the truly second order corrected density  $\rho^{(0)} + \rho^{(2)}$ . This would mean that the infinite summation performed indirectly by solving the Dyson equation has no effect, or at least not on the density. This is confirmed by comparing the nuclear attraction  $V_{\text{Ne}}$  and the kinetic energy  $T$  for GF(2) and MP(2). The energy contributions are almost the same in both methods and also close to the CI results.

Now the two-electron energy will be examined in more detail, i.e., the two terms  $V_{\text{static}}$  and  $\frac{1}{2} \text{Tr} \Gamma^{\text{corr}}$  that constitute  $V_{ee}$ . The term  $V_{\text{static}}$  is defined as  $V_{\text{static}} = V_{ee} - \frac{1}{2} \text{Tr} \Gamma^{\text{corr}}$  and accounts for the Hartree–Fock like part of the electron repulsion energy. Again comparing MP(2) and GF(2) one notices that there is no difference in the true-correlation contribution  $\frac{1}{2} \text{Tr} \Gamma^{\text{corr}}$  and consequently the term  $V_{\text{static}}$  is totally responsible for the difference in the total energy between MP(2) and GF(2). This is due to the fact that  $V_{\text{static}}$  contains  $\text{Tr} \Gamma^2$  in the case of MP(2) and  $\frac{1}{2} \text{Tr} \Gamma^2$  in the case of GF(2), and not to the fact that  $\Gamma^2$  is slightly different in GF(2) and MP(2) as Table I shows. Since  $\Gamma^1$  is fully determined by the density this further confirms that the Dyson summation has almost no effect on the density in the case of the He atom. It also has hardly any effect on the true correlation contribution.

Table II contains the results for the Be atom, the CI refers to a SDCI from 13 reference configurations as in I. Comparing MP(2) and GF(2) almost the same conclusions as for He can be drawn: there is no significant difference for



TABLE I. Ground state energies for the He atom (in  $E_h$ ). Vertical: Hartree–Fock (HF), second order Møller–Plesset (MP(2)), second order Green's function (GF(2)), and configuration interaction (CI). Horizontal: electron–nucleus attraction  $V_{Ne}$ , kinetic energy  $T$ , total one-electron energy  $h = V_{Ne} + T$ , density dependent correction to the electron–electron repulsion  $\frac{1}{2} \text{Tr } \Gamma^1$ , total electron–electron repulsion  $V_{static}$ , dynamic correlation energy  $\frac{1}{2} \text{Tr } \Gamma^{corr}$ , total electronic energy  $E^{el} = h + V_{ee}$ . The nuclear repulsion is denoted as  $V_{NN}$  and the density obtained from the second order Green's function as  $\rho^{Dyson(2)}$ .  $\text{Tr } \rho^{Dyson(2)} = 2.00016$ .

	$V_{Ne}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{static}$	$\frac{1}{2} \text{Tr } \Gamma^{corr}$	$V_{ee}$	$E^{el}$
HF	−6.7462	2.8600	−3.8862	0	1.0251	0	1.0251	−2.8610
MP(2)	−6.7567	2.8973	−3.8594	0.0043	1.0336	−0.0706	0.9630	−2.8963
GF(2)	−6.7569	2.8974	−3.8596	0.0043	1.0295	−0.0705	0.9590	−2.9006
CI	−6.7514	2.9024	−3.8490	0.0052	1.0355	−0.0884	0.9471	−2.9019

the terms  $V_{Ne}$  to  $\frac{1}{2} \text{Tr } \Gamma^{corr}$ ; the difference in  $V_{ee}$  and  $E^{el}$  is fully attributable to an extra  $\frac{1}{2} \text{Tr } \Gamma^2$  contribution. This difference is much bigger than that in the case of the He atom due to the fact that the density dependent term  $\frac{1}{2} \text{Tr } \Gamma^1$  is not small now. The conclusions in I can now be repeated for MP(2): the rather accurate value for the total energy is due to a fortuitous cancellation in the terms that constitute the electron–electron repulsion energy. It was shown in I that the radial distribution of the electron density as calculated for GF(2) locally differs considerably from the corresponding CI charge distribution. This wrong behavior is of course due to the near degeneracy of the system which cannot be accounted for in the reference single-determinant wave function. The MP(2) density very likely suffers from the same drawback.

The conclusions to be drawn from the results for the LiH molecule in Table III are essentially identical to those drawn from the results from Table I for the He atom. This conforms to what one reasonably would expect since both systems are well described by Hartree–Fock theory. Again, as in He the MP(2) results are almost identical to the GF(2) results and very close to the CI results. The slightly better GF(2) electronic energy as compared to MP(2) is once more due to the different way that  $\text{Tr } \Gamma^1$  enters the energy expressions. This effect is small though significant.

## B. The hydrogen molecule

The minimal basis used in Sec. III provides exact results in the limiting case of  $R \rightarrow \infty$  but is obviously inadequate at smaller distances and is in particular insufficient to describe the system at the equilibrium distance  $R_e = 1.4008a_0$ . Therefore calculations have also been performed in the larger basis that was used in I which consists of 34 basis func-

tions. In I it has been shown that at distances  $R < R_e$  the results from  $G^{Dyson(2)}(\omega)$  are accurate. However, with  $R$  increasing to values greater than  $R_e$  the results soon become inaccurate, though the largest distance used was still rather small:  $3.0a_0$ . One may ask what happens with for instance the total energy as obtained from  $G^{Dyson(2)}(\omega)$ , taken in the larger basis now, when pulling the nuclei apart to infinity. From the results of I one might expect that  $E^{Dyson(2)}(\omega)$  would become very bad at  $R \rightarrow \infty$ . However, the model of Sec. III shows that in a minimal basis  $E^{Dyson(2)}$  becomes exact in this limit, and one would expect this result to hold approximately on augmenting the basis.

It turns out that the difference between the minimal basis and a larger basis is to be found in the orbitals. In a minimal basis there is only one possible set of orbitals namely the symmetry determined set of orbitals (3.6) and (3.7) which in this case are constructed from the atomic hydrogen orbitals and differ therefore from the real Hartree–Fock orbitals. A larger basis will in general be flexible enough to describe the real Hartree–Fock orbitals. As a consequence the density calculated from the gerade and ungerade Hartree–Fock orbitals will still be too diffuse even if the occupation numbers are both 0.5 since the orbitals are too diffuse. Therefore it is expected that  $E^{Dyson(2)}$  will not be exact in the larger basis at  $R \rightarrow \infty$ .

In Fig. 1  $E^{Dyson(2)}$  and  $E^{CI}$  as well as  $E^{HF}$  and  $E^{HF} + E^{(2)}$  are plotted against the internuclear distance. Comparing  $E^{Dyson(2)}$  and  $E^{CI}$  one notes that at distances smaller than approximately the equilibrium distance  $E^{Dyson(2)}$  is very accurate. This is a consequence of the well-known fact that in this region the Hartree–Fock approximation is good which implies a quick convergence of the perturbation expansion of the correlation energy. With increasing

TABLE II. Ground state energies for the Be atom. For the meaning of the row and column headings see Table I.  $\text{Tr } \rho^{Dyson(2)} = 4.005192$ .

	$V_{Ne}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{static}$	$\frac{1}{2} \text{Tr } \Gamma^{corr}$	$V_{ee}$	$E^{el}$
HF	−33.6279	14.5696	−19.0582	0	4.4886	0	4.4886	−14.5697
MP(2)	−33.6712	14.6359	−19.0353	0.0228	4.5342	−0.1371	4.3971	−14.6382
GF(2)	−33.6790	14.6370	−19.0419	0.0256	4.5142	−0.1366	4.3776	−14.6643
CI	−33.6791	14.6469	−19.0322	0.0476	4.5815	−0.2075	4.3740	−14.6582

TABLE III. Ground state energies for the LiH molecule. For the meaning of the row and column headings see Table I.  $V_{NN} = 0.99502$ ,  $\text{Tr } \rho^{\text{Dyson}(2)} = 4.00112$ .

	$V_{\text{Ne}}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{cl}}$
HF	-20.4538	7.9913	-12.4625	0	3.4831	0	3.4831	-8.9794
MP(2)	-20.4625	8.0468	-12.4139	0.0071	3.4972	-0.1254	3.3717	-9.0422
GF(2)	-20.4625	8.0472	-12.4153	0.0077	3.4908	-0.1252	3.3656	-9.0498
CI	-20.4467	8.0583	-12.3884	0.0087	3.4999	-0.1663	3.3336	-9.0548

$R E^{\text{Dyson}(2)}$  deviates more and more from  $E^{\text{CI}}$ , the difference reaching a maximum at about  $R = 5.0a_0$ . This is because the Hartree–Fock starting point is now bad and perturbation theory is not able to fully correct this deficiency. At larger distances the Dyson summation becomes effective causing the  $E^{\text{Dyson}(2)}$  curve to bend downwards and eventually settling parallel to the  $E^{\text{CI}}$  curve, though at a somewhat lower value.

The characteristics of the  $E^{\text{HF}} + E^{(2)}$  curve, referred to as the MP(2) curve from now on are the same as those for  $E^{\text{Dyson}(2)}$  up to the crossing point at  $R = 10a_0$  except that it is shifted up an amount  $E^{\text{HF}} + E^{(2)} - E^{\text{Dyson}(2)} \approx \frac{1}{2} \text{Tr } \Gamma^1 \sim \frac{1}{2} \text{Tr } \Gamma^{1(2)}$ . From the crossing point onward the MP(2) energy starts to diverge due to the degeneracy of the eigenvalues corresponding to the gerade and ungerade orbitals, cf. Eq. (3.30).

The results of calculations at  $R = 1.4008a_0$ ,  $5.0a_0$ ,  $10a_0$ , and  $30a_0$  are collected in Tables IV–VII. At the equilibrium distance the situation is like that in the case of the He atom: MP(2) as well as GF(2) produce rather accurate results. The difference in  $E^{\text{cl}}$  and  $V_{ee}$  is determined by the term  $\frac{1}{2} \text{Tr } \Gamma^1$ . There is no significant difference in the one-electron terms including  $\frac{1}{2} \text{Tr } \Gamma^1$ , indicating no effect of the Dyson

summation. This changes at  $5.0a_0$ ; the MP(2) one-electron terms now start to differ from their GF(2) equivalents. The difference in MP(2) and GF(2) total energy increase but is still determined by  $\frac{1}{2} \text{Tr } \Gamma^1$ . Beyond  $10a_0$  the situation changes drastically. The GF(2) results now come closer to the CI results whereas the MP(2) results differ more, compared to the situation at  $5.0a_0$ . Near the crossing point the MP(2) total energy is close to the CI value but this is clearly due to fortuitous cancellation since  $h$  and  $V_{ee}$  are by no means close to the CI value. At  $30a_0$  the situation is even more extreme. The HF, CI, and GF(2) numbers have reached their limiting values, the MP(2) results are now meaningless.

### C. Ne, HF, H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub>

We now turn to the results for the ten electron series Ne, HF, H<sub>2</sub>O, NH<sub>3</sub>, and CH<sub>4</sub> collected in Tables VIII–XII. For Ne the  $5s4p$  contracted Gaussian basis set from Dunning<sup>17</sup> was used, augmented with two  $d$  functions, exponents 1.89<sup>18</sup> and 0.8,<sup>19</sup> and one  $f$  function, exponent 2.5,<sup>20</sup> resulting in 34 functions in total. On the H atoms of HF, NH<sub>3</sub> and CH<sub>4</sub> we used the  $3s$  set of Dunning<sup>21</sup> augmented with a  $p$  function with exponent 1.0. For HF the  $7s4p2d$  set from Lie and Clementi<sup>22</sup> augmented with an  $f$  function with exponent 1.0 was used, yielding 42 functions. The HF internuclear distance,  $1.733a_0$ , was taken from Urban *et al.*<sup>23</sup> For the H<sub>2</sub>O molecule we adopted the basis and geometry that was denoted as ‘basis 3’ in I, which consists of 44 functions. For NH<sub>3</sub> and CH<sub>4</sub> the  $5s3p$  sets from Dunning,<sup>21</sup> were taken. These sets were augmented with a  $d$  function with exponent 0.85<sup>23</sup> in the case of NH<sub>3</sub> and with exponent 0.626<sup>24</sup> in the case of CH<sub>4</sub>. For NH<sub>3</sub> this resulted in 38 functions, the geometry was taken from Ref. 23. The CH<sub>4</sub> this resulted in 44 functions and the experimental C–H distance<sup>25</sup> of  $2.065a_0$  was used. For all these systems a MRSD–CI of reasonable accuracy, i.e., 10 to 15 reference configurations, was performed.

In the results discussed in Secs. IV A and IV B the GF(2) total energy was always lower than the corresponding MP(2) energy. The difference GF(2)–MP(2) turned out to be  $-\frac{1}{2} \text{Tr } \Gamma^1$  where  $\frac{1}{2} \text{Tr } \Gamma^1$  always was a positive number. This is different in the series of calculations presently under consideration. For the system Ne, HF, and H<sub>2</sub>O the contribution  $\frac{1}{2} \text{Tr } \Gamma^1$  is negative resulting in an MP(2) total energy that is lower than GF(2). For the systems NH<sub>3</sub> and CH<sub>4</sub> the  $\frac{1}{2} \text{Tr } \Gamma^1$  term is positive again.

This effect can be interpreted as follows. It is well known that the Hartree–Fock electron density is too diffuse. Correlating the motion of the electrons will contract the density.

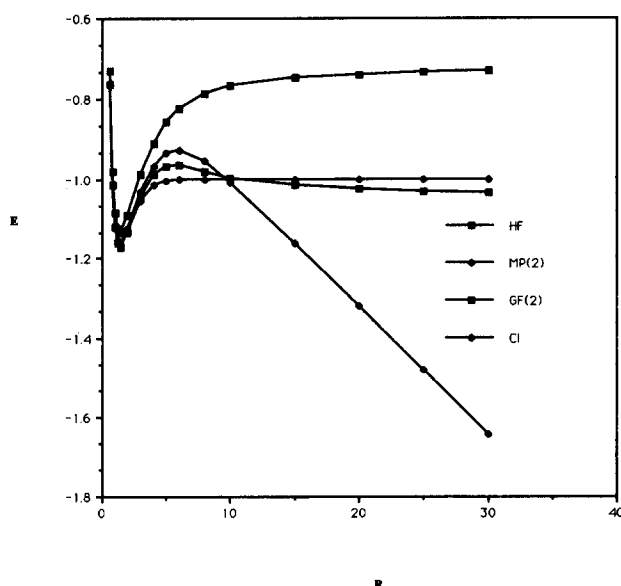


FIG. 1. The total molecular ground state energy  $E$  (in  $E_h$ ) of the H<sub>2</sub> molecule from Hartree–Fock (HF), second order Møller–Plesset (MP(2)), second order Green's function (GF(2)), and configuration interaction (CI) calculations as a function of the internuclear distance  $R$  (in  $a_0$ ).

TABLE IV. Ground state energies for the H<sub>2</sub> molecule at  $R = R_0 = 1.4008a_0$ . For the meaning of the row and column headings see Table I.  $V_{NN} = 0.7139E_h$ ,  $\text{Tr } \rho^{\text{Dyson}(2)} = 2.000\ 56$ .

	$V_{Ne}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{el}}$
HF	-3.6309	1.1253	-2.5056	0	0.6582	0	0.6582	-1.8473
MP(2)	-3.6439	1.1579	-2.4860	0.0059	0.6701	-0.0628	0.6072	-1.8788
GF(2)	-3.6447	1.1582	-2.4865	0.0061	0.6643	-0.0627	0.6016	-1.8849
CI	-3.6474	1.1722	-2.4752	0.0096	0.6772	-0.0884	0.5888	-1.8864

TABLE V. Ground state energies for the H<sub>2</sub> molecule at  $R = 5.0a_0$ . For the meaning of the row and column headings see Table I.  $V_{NN} = 0.2000 E_h$ ,  $\text{Tr } \rho^{\text{Dyson}(2)} = 2.014\ 51$ .

	$V_{Ne}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{el}}$
HF	-2.0726	0.6502	-1.4224	0	0.3635	0	0.3635	-1.0589
MP(2)	-2.2474	0.8261	-1.4213	0.0378	0.4392	-0.1536	0.2856	-1.1357
GF(2)	-2.2327	0.8059	-1.4268	0.0345	0.3980	-0.1385	0.2595	-1.1673
CI	-2.3839	0.9770	-1.4069	0.0985	0.5026	-0.2992	0.2034	-1.2035

TABLE VI. Ground state energies for H<sub>2</sub> molecule at  $R = 10.0a_0$ . For the meaning of the row and column headings see Table I.  $V_{NN} = 0.1000 E_h$ ,  $\text{Tr } \rho^{\text{Dyson}(2)} = 2.050\ 10$ .

	$V_{Ne}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{el}}$
HF	-1.8826	0.7094	-1.1732	0	0.3060	0	0.3060	-0.8673
MP(2)	-2.4673	1.2212	-1.2461	0.1574	0.6209	-0.4840	0.1368	-1.1093
GF(2)	-2.1797	0.9630	-1.2167	0.0619	0.3679	-0.2473	0.1205	-1.0962
CI	-2.2000	1.0000	-1.2000	0.0800	0.4125	-0.3125	0.1000	-1.1000

TABLE VII. Ground state energies for the H<sub>2</sub> molecule at  $R = 30.0a_0$ . For the meaning of the row and column headings see Table I.  $V_{NN} = 0.333\ 33 E_h$ ,  $\text{Tr } \rho^{\text{Dyson}(2)} = 2.0623$ .

	$V_{Ne}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{el}}$
HF	-1.7600	0.7203	-1.0397	0	0.2747	0	0.2747	-0.7650
MP(2)	-3.7326	2.3818	-1.3508	0.6111	1.4969	-1.8222	-0.3253	-1.6761
GF(2)	-2.0857	0.9982	-1.0875	0.0497	0.3244	-0.3034	0.0210	-1.0665
CI	-2.0667	1.0000	-1.0667	0.0455	0.3458	-0.3125	0.0333	-1.0333

TABLE VIII. Ground state energies for the Ne atom. For the meaning of the row and column headings see Table I.  $\text{Tr } \rho^{\text{Dyson}(2)} = 10.002\ 29$ .

	$V_{Ne}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{el}}$
HF	-311.1278	128.5420	-182.5859	0	54.0454	0	54.0454	-128.5404
MP(2)	-310.6912	128.5993	-182.0920	-0.1064	53.8327	-0.5624	53.2703	-128.8216
GF(2)	-310.6985	128.5972	-182.1013	-0.1014	53.9440	-0.5616	53.3824	-128.7188
CI	-310.8923	128.6962	-182.1961	-0.0574	53.9304	-0.5542	53.3761	-128.8200

TABLE IX. Ground state energies for the HF molecule. For the meaning of the row and column headings see Table I.  $V_{NN} = 4.9729 E_h$ ,  $\text{Tr } \rho^{\text{Dyson}(2)} = 10.004\ 88$ .

	$V_{Ne}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{el}}$
HF	-250.6360	100.0328	-150.6032	0	45.3426	0	45.3426	-105.2606
MP(2)	-250.2715	100.1595	-150.1119	-0.1005	45.1416	-0.5805	44.5610	-105.5509
GF(2)	-250.2831	100.1565	-150.1267	-0.0929	45.2497	-0.5795	44.6702	-105.4565
CI	-250.4817	100.2400	-150.2416	-0.0411	45.2598	-0.5635	44.6945	-105.5471

TABLE X. Ground state energies for the H<sub>2</sub>O molecule. For the meaning of the row and column headings see Table I.  $V_{\text{NN}} = 9.1972 E_h$ ,  $\text{Tr } \rho^{\text{Dyson}(2)} = 10.00487$ .

	$V_{\text{Ne}}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{el}}$
HF	-199.0627	76.0007	-123.0620	0	37.8201	0	37.8201	-85.2419
MP(2)	-198.9489	76.2316	-122.7173	-0.0405	37.7390	-0.5272	37.2118	-85.5055
GF(2)	-198.9687	76.2328	-122.7359	-0.0311	37.7890	-0.5264	37.2626	-85.4733
CI	-199.0175	76.2418	-122.7758	-0.0158	37.7877	-0.5152	37.2725	-85.5033

TABLE XI. Ground state energies for the NH<sub>3</sub> molecule. For the meaning of the row and column headings see Table I.  $V_{\text{NN}} = 11.9630 E_h$ ,  $\text{Tr } \rho^{\text{Dyson}(2)} = 10.00277$ .

	$V_{\text{Ne}}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{el}}$
HF	-155.8153	56.1686	-99.6467	0	31.4734	0	31.4734	-68.1733
MP(2)	-156.0714	56.4890	-99.5824	0.0772	31.6279	-0.4376	31.1904	-68.3920
GF(2)	-156.0844	56.4910	-99.5934	0.0827	31.5561	-0.4367	31.1194	-68.4740
CI	-155.9670	56.4439	-99.5230	0.0536	31.5799	-0.4567	31.1233	-68.3998

TABLE XII. Ground state energies for the CH<sub>4</sub> molecule. For the meaning of the row and column headings see Table I.  $V_{\text{NN}} = 13.3919 E_h$ ,  $\text{Tr } \rho^{\text{Dyson}(2)} = 10.00271$ .

	$V_{\text{Ne}}$	$T$	$h$	$\frac{1}{2} \text{Tr } \Gamma^1$	$V_{\text{static}}$	$\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$	$V_{ee}$	$E^{\text{el}}$
HF	-119.7844	40.1378	-79.6466	0	26.0469	0	26.0469	-53.5997
MP(2)	-120.0220	40.3861	-79.6358	0.0893	26.2255	-0.3788	25.8467	-53.7891
GF(2)	-120.0382	40.3906	-79.6477	0.0955	26.1424	-0.3792	25.7632	-53.8844
CI	-119.9273	40.3650	-79.5623	0.0670	26.1802	-0.4233	25.7569	-53.8054

As a result the static part of the electron–electron repulsion,  $V_{\text{static}}$ , will increase. This effect is described by the term  $\frac{1}{2} \text{Tr } \Gamma^1$  which is therefore usually positive. If, however, the electron density expands by correlating the electrons the contributions of  $\frac{1}{2} \text{Tr } \Gamma^1$  will lower the electron–electron repulsion and as a result the MP(2) total energy is lower than the GF(2) energy. It can immediately be verified from Table VIII–XII that for the systems Ne, HF, and H<sub>2</sub>O the nuclear attraction energy  $V_{\text{Ne}}$  rises relative to Hartree–Fock which also indicates an expanding density whereas it falls in NH<sub>3</sub> and CH<sub>4</sub> indicating a contracting density.

In all these 10 electron systems the following observations hold.

(1) There is little difference between MP(2) and GF(2) for all terms except  $V_{\text{static}}$ ,  $V_{ee}$ , and  $E^{\text{el}}$ . This means in particular that  $\rho^{\text{Dyson}(2)}$  differs very little from  $\rho^{(0)} + \rho^{(2)}$  since the difference in one-electron terms (including  $\Gamma^1$ ) is completely determined by the density. Furthermore this means that the inclusion of terms

$$\rho^{2(n)} = \frac{1}{2\pi i} \oint d\omega G^{(0)} [\Sigma^{(2)} G^{(0)}]^n, \quad n = 1, 2, \dots, \infty$$

in the density is not very effective i.e., the Dyson summation could as well be omitted and the whole series be replaced by the second order term only as far as the density is concerned.

(2) The correction to the kinetic energy is described reasonably well and usually somewhat better than correction to  $V_{\text{Ne}}$  by both MP(2) and GF(2).

(3) The true correlation contribution  $\frac{1}{2} \text{Tr } \Gamma^{\text{corr}}$  as calculated from MP(2) as well as from GF(2) is accurate compared to CI and accounts for the greatest part of the correction to  $V_{ee}$ .

(4) The difference in the  $V_{ee}$  correction as calculated from MP(2) and GF(2) is fully determined by the extra contribution  $\frac{1}{2} \text{Tr } \Gamma^1$  in MP(2). GF(2) consistently yields a better value for  $V_{ee}$  than MP(2).

(5) The difference in the total energy is determined by the difference in  $V_{ee}$  which results in too high a value for  $E^{\text{Dyson}(2)}$  for Ne, HF, and H<sub>2</sub>O where  $\frac{1}{2} \text{Tr } \Gamma^1$  is negative and too low a value for  $E^{\text{Dyson}(2)}$  in the case of NH<sub>3</sub> and CH<sub>4</sub> where  $\frac{1}{2} \text{Tr } \Gamma^1$  is positive.

(6) Both MP(2) and GF(2) yields a relatively inaccurate  $V_{\text{Ne}}$ . The error in this term is of about the same magnitude as  $\frac{1}{2} \text{Tr } \Gamma^1$  but has the opposite sign.

(7) The MP(2) electronic energy is closer to the CI than GF(2). Following observations (5) and (6) this is attributable to cancellation of  $V_{\text{Ne}}$  against  $\frac{1}{2} \text{Tr } \Gamma^1$  in MP(2) which does not take place in GF(2).

In conclusion it can be said that the difference between MP(2) and GF(2) is determined by the extra term  $\frac{1}{2} \text{Tr } v^{\text{HF}}(\rho^{\text{HF}}) \Delta \rho^{(2)} = \frac{1}{2} \text{Tr } \Gamma^{1(2)}$  that is present in Eq. (2.42) and not by the fact that in GF(2) higher than second order terms are included. This yields a consistently better electron repulsion energy  $V_{ee}$  from GF(2). However, as a consequence of the less satisfactory description of  $V_{\text{Ne}}$  and

therefore of  $h$ , by both MP(2) and GF(2), the better  $V_{ee}$  value of GF(2) implies a worse value for the total energy  $E^{\text{el}}$ .

## V. CONCLUSIONS

The relation between Møller–Plesset and Green's function total energies has been established. This relation has been analyzed in detail for the second order. It has been pointed out that if in the general energy formula (2.17) the Green's function  $G(\omega)$  is replaced by the second order term  $G^{(2)}(\omega)$  one does not obtain the second order energy  $E^2$ . In order to obtain  $E^{(2)}$  one also has to replace the one-electron operator  $h$  by the Fock operator  $F$ . One can view this as a consequence of the fact that  $h$  is not of zero order but  $F$  is. This causes the energy expression as obtained from GF(2) to differ an amount  $\frac{1}{2} \text{Tr } v^{\text{HF}}[\rho^{\text{HF}}]\Delta\rho^{(2)}$  from the MP(2) correction.

An expression for the Green's function has been obtained for the  $\text{H}_2$  molecule in a minimal basis. From this it has been shown that the Green's function obtained from the second-order self-energy becomes exact in the limit of infinite internuclear distance and produces the correct number ( $-1.0E_h$ ) for the total energy. This contrasts sharply with the Møller–Plesset energy which diverges in this limit. The model is an example of the power of the Dyson summation.

Although the Green's function for the  $\text{H}_2$  molecule in a larger basis does not become exact (within the basis) at  $R \rightarrow \infty$  it does not suffer from divergences and produces an acceptable value for the total energy whereas MP(2) diverges. On the other hand among the cases studied here the hydrogen molecule at long internuclear distances is the only system where the effect of the Dyson summation is truly significant. In all other cases the difference between the MP(2) energy  $E^{(2)}$  and the correction  $E^{\text{Dyson}(2)}$  obtained from the Green's function is almost completely determined by the fact that  $E^{(2)}$  contains an extra term  $\frac{1}{2} \text{Tr } \Gamma^1$  relative to  $E^{\text{Dyson}(2)}$ .

It is not possible to decide from theory whether or not this extra term should be included. One could argue that it should be included in  $E^{\text{Dyson}(2)}$  to make it more consistent in the order of the perturbation. But on the other hand the Green's function method is intrinsically inconsistent in orders when partial Dyson summations are used. So it seems better to let numerical calculations settle the issue. However, the results presented here do not provide sufficient evidence as to what is the best way to calculate the energy correction.

In all the systems studied in this paper GF(2) yields a better value for the electron repulsion energy  $V_{ee}$  than

MP(2). For the systems He, Be, LiH, and  $\text{H}_2$  the GF(2) total energy  $E^{\text{el}}$  is better than the corresponding MP(2) number. However, as shown by the results in Sec. III C, a better  $V_{ee}$  does not necessarily imply a better value for the total energy. Since also in all systems there is no significant difference in the one-electron corrections from GF(2) and MP(2) one might argue that GF(2) is superior to MP(2) even though the total energy obtained from GF(2) may be worse.

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