

# Nonconventional Partitioning of the Many-Body Hamiltonian for Studying Correlation Effects

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**ABSTRACT:** For the treatment of electron correlation, one most often uses the Møller–Plesset (MP) partition which defines the zero-order Hamiltonian through the spectral resolution of the Fockian. We investigate how the MP partitioning can be improved while still using the Hartree–Fock (HF) reference state; and how the HF wave function can be substituted by a correlated one preserving the formal simplicity of the HF-based approach. To improve the  $MP^n$  result, we introduce a fine tuning of energy denominators replacing the HF orbital energies with the ionization potentials obtained from the second-order Dyson equation. As this equation usually tends to close the gaps, a slight decrease of the denominators is expected, inducing an improvement of low-order correlation energies. We keep the simplicity of the MP partitioning and handle Dyson corrections as simple level shifts. Substituting doubly filled HF orbitals by strongly orthogonal geminals, one introduces a correlated reference state which is variational, size-consistent, and properly describes single-bond dissociation. This wave function, the antisymmetrized product of strongly orthogonal geminals (APSG), offers a good starting point for further corrections. We show that the use of an APSG reference state in the equation-of-motion technique leads to Tamm–Dankoff approach (TDA) equations which account for correlation effects in electronic excitation energies. © 1998 John Wiley & Sons, Inc. *Int J Quant Chem* 70: 571–581, 1998

**Key words:** partitioning; level shift; quasi-degenerate PT; Dyson equation; geminals; excited states

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## Introduction

**P**erturbation theory, with a variety of its formalisms [1], has been a powerful tool for taking small interactions into account. In some cases the splitting of the total Hamiltonian comes up naturally, being motivated by the physics of the problem (cf. molecules in external fields), while in other situations the partitioning is ambiguous and can only be governed by mathematical and numerical considerations. An example for this latter case is represented by many-body perturbation theory (MBPT) as applied to the calculation of electronic energies in molecules. Here the partitioning of the total electronic Hamiltonian is motivated by selecting a zeroth order which is easily soluble—a practical rather than unambiguous factor.

In the most widely used partitioning of this type one chooses the the Hartree–Fock (HF) level to define the zeroth order. This choice still allows for various possibilities. The most straightforward idea is to consider the diagonal elements of the configuration interjection (CI) matrix as zero-order levels, while the off-diagonals represent the perturbation (Epstein–Nesbet, EN, partitioning [2, 3]). Much better numerical results are obtained from the Møller–Plesset (MP) partitioning [4], where one chooses the Fockian as zeroth-order operator. Though the  $n$ th order (MP $n$ ) corrections do not offer an upper bound to the energy, general experience tells us that they usually underestimate the correlation energy for small  $n$ .

Standard MP $n$  corrections with a simple closed-shell reference state are applicable only if the restricted HF determinant is an acceptable approximation. Dissociation curves or other quasidegenerate situations require a multireference approach [5–14], special damping techniques [15–17], or a repartitioning of the Hamiltonian by a suitable level shift [10, 18–20] to remove quasidegeneracies from the zeroth-order spectrum. A different sort of repartitioning has been applied by Kapuy et al. [21–23] in their MBPT with localized molecular orbitals (LMOs): They select the diagonal elements of the Fockian in LMO basis as zero-order energies and treat the off-diagonals as one-electron perturbations.

In approximating the exact energy, it is not necessary to start at the HF level. One may quote

the old idea of the PCILO method [24] where approximate, strictly localized MOs are used at the zeroth order. Correlation and delocalization effects are treated by PT on an equal footing, thus the zeroth-order approximation in PCILO is weaker than HF. Oppositely, one may use a zeroth order which is better than HF (cf. the multireference PT approaches [5–10] or attempts to improve geminal approximations perturbatively [25–30]).

In this study we shall investigate two kinds of repartitioning in MBPT. In the following section, level shifts will be introduced within the framework of closed-shell MP theory, while in the third section the use of the antisymmetrized product of strongly orthogonal geminals (APSG) reference state will be discussed. A small number of preliminary test calculations will be reported in both cases.

## Repartitioning by Level Shifts

### REAL SHIFTS

In MP theory, one considers the partitioning

$$\hat{H} = \sum_i \epsilon_i a_i^+ a_i + \hat{W}, \quad (1)$$

where  $\hat{H}$  is the total many-body electronic Hamiltonian,  $\epsilon_i$ 's are the canonical Hartree–Fock orbital energies, while  $a_i^+$  and  $a_i$  are creation and annihilation operators for molecular spin-orbitals.

Applying a shift  $\lambda_i$  to level  $i$  corresponds to the repartitioning

$$\hat{H} = \sum_i \epsilon_i a_i^+ a_i + \hat{W}', \quad (2)$$

where

$$\epsilon_i = \epsilon_i + \lambda_i \quad (3)$$

are the shifted one-particle energies.

Using Eq. (2), the second-order correction becomes

$$\Delta E^{[2]} = -\frac{1}{4} \sum_{pq,rs} \frac{[pq||rs]^2}{\epsilon_r + \epsilon_s - \epsilon_p - \epsilon_q} \quad (4)$$

with usual notations,  $p, q$  referring to occupied,  $r, s$  to virtual levels. The third-order correction undergoes a similar modification and, due to the diagonal perturbation represented by the level shift

operators, it is augmented by the term

$$-\frac{1}{4} \sum_{pq,rs} \frac{[rs||pq]^2}{(\epsilon_r + \epsilon_s - \epsilon_p - \epsilon_q)^2} (\lambda_r + \lambda_s - \lambda_p - \lambda_q). \quad (5)$$

Such level shifts have been discussed previously by several authors [10, 18–20]. Recently [31], we started to investigate the idea of replacing  $\epsilon_i$  with correlation-corrected ionization potentials or electron affinities  $\epsilon_i$  obtained from the second-order inverse Dyson equation:

$$\begin{aligned} \epsilon_i = \epsilon_i + \frac{1}{2} \sum_{pqr} \frac{[ir||pq]^2}{\epsilon_i + \epsilon_r - \epsilon_p - \epsilon_q} \\ + \frac{1}{2} \sum_{prs} \frac{[ip||rs]^2}{\epsilon_i + \epsilon_p - \epsilon_r - \epsilon_s}. \end{aligned} \quad (6)$$

This formula originates from the theory of one-particle Green's functions [32–35] by truncating the self-energy at second order. Although it is not a good approximation to obtain accurate ionization potentials and electron affinities, it shifts the Koopmans values in a way to reduce energy gaps [e.g., highest occupied molecular orbital and lowest unoccupied molecular orbital (HOMO–LUMO) differences] in most cases. This feature of Eq. (6) is utilized in solid-state theory to compute correlation-corrected band structures [36, 37]. The slightly smaller energy denominators, received by substituting the Koopmans values  $\epsilon_i$  by the Dyson-corrected ones  $\epsilon_i$ , yield slightly larger MP2 corrections, thus a larger fraction of the correlation energy.

The nonlinear equations (6) for  $\epsilon_i$  have to be solved iteratively. This is straightforward\* if the root of the equation is far from all singularities (poles). In the general case, however, one has to introduce a complex damping of strength  $\eta$

$$\begin{aligned} \epsilon_i = \epsilon_i + \frac{1}{2} \sum_{pqr} \frac{[ir||pq]^2}{\epsilon_i + \epsilon_r - \epsilon_p - \epsilon_q - i\eta} \\ + \frac{1}{2} \sum_{prs} \frac{[ip||rs]^2}{\epsilon_i + \epsilon_p - \epsilon_r - \epsilon_s + i\eta}, \end{aligned} \quad (7)$$

where  $\eta$  tends to zero. Separating the real and imaginary parts of this equation one may arrive at

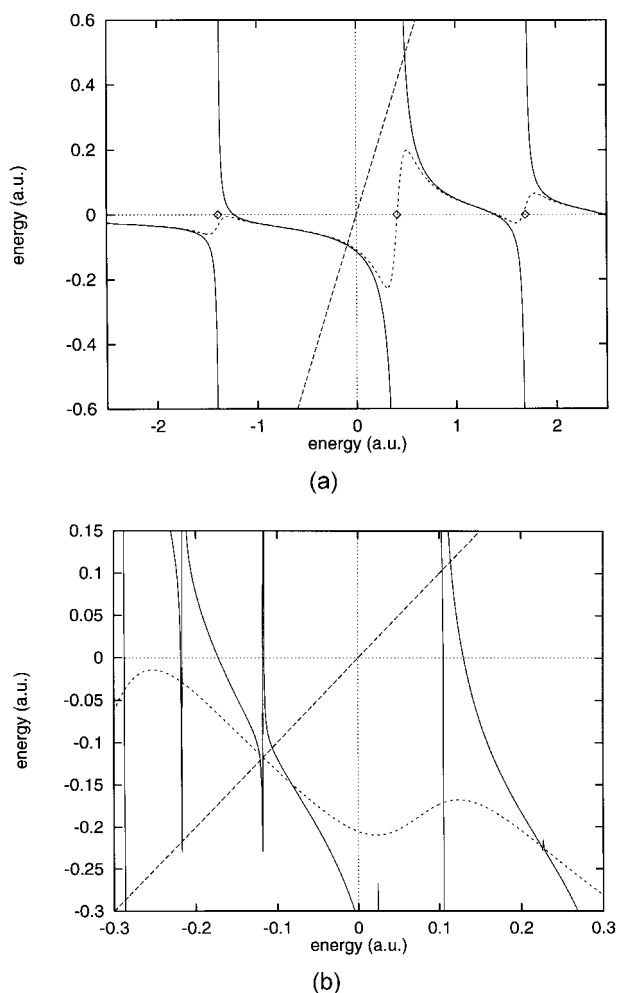
\* 50% damping is usually sufficient to ensure convergence of the standard iterative series.

the following damped expression:

$$\begin{aligned} \epsilon_i = \epsilon_i + \frac{1}{2} \sum_{pqr} \frac{[ir||pq]^2 (\epsilon_i + \epsilon_r - \epsilon_p - \epsilon_q)}{(\epsilon_i + \epsilon_r - \epsilon_p - \epsilon_q)^2 + \eta^2} \\ + \frac{1}{2} \sum_{prs} \frac{[ip||rs]^2 (\epsilon_i + \epsilon_p - \epsilon_r - \epsilon_s)}{(\epsilon_i + \epsilon_p - \epsilon_r - \epsilon_s)^2 + \eta^2}, \end{aligned} \quad (8)$$

which can be successfully used to avoid false roots and to ensure convergence. An example for the use of Eq. (8) is shown in Figure 1.

An even simpler, iteration-free, correction to the Koopmans values is obtained by standard MP2



**FIGURE 1.** Solution of the second-order Dyson equation  $\epsilon = f(\epsilon)$  with (dashed line) and without (solid line) damping. The straight dashed line is the left-hand side while the curves are plots of  $f(\epsilon)$  at the right-hand side. (a) H<sub>2</sub> molecule 3-21G\*\* basis, HOMO; (b) N<sub>2</sub> molecule 6-3111G\*\* basis, MO No.21.

theory to ionization energies

$$\epsilon_i^{\text{MP2}} = \epsilon_i + \frac{1}{2} \sum_{pqr} \frac{[ir||pq]^2}{\epsilon_i + \epsilon_r - \epsilon_p - \epsilon_q} + \frac{1}{2} \sum_{prs} \frac{[ip||rs]^2}{\epsilon_i + \epsilon_p - \epsilon_r - \epsilon_s}. \quad (9)$$

Clearly, this corresponds to the first iteration of Eq. (6). This formula has also been used to correct band structures in periodic systems [38–40].

### IMAGINARY LEVEL SHIFTS

Similarly to the damping of Dyson equation, cf. Eq. (7), one can introduce an imaginary level shift in the energy denominator of the MP2 formula

$$\Delta E_{\text{complex}}^{[2]} = - \sum_k \frac{|W_{0k}|^2}{E_k - E_0 + i\Gamma_k}. \quad (10)$$

While in the case of Dyson equation the actual value of  $\eta$  is immaterial as, after achieving convergence to the correct root, the  $\eta \rightarrow 0$  limit has to be considered, in the case of Eq. (10) a suitable choice for  $\Gamma$  has to be made, in order to make Eq. (10) valid in quasi-degenerate (QD) situations. Another question is how to extract a real number from  $\Delta E_{\text{complex}}^{[2]}$  of Eq. (10). In Ref. [16], we took the term-by-term absolute value of this expression and determined  $\Gamma$  by requiring the resulting formula to be exact for a fully degenerate two-level system [16] ( $\Gamma_k = W_{0k}$ ), or by fitting  $\Gamma$  to the relevant term of the fourth-order expression [41, 42] ( $\Gamma_k = 2W_{0k}$ ). In a recent study, Forsberg and Malmqvist [43] took the real component of Eq. (10), just like Eq. (8). This has the advantage that it can also be

applied for excited states (negative excitation energies), but has the disadvantage that it kills a fully degenerate term completely, thus it is inadequate, e.g., for a degenerate two-level system. Forsberg and Malmqvist do not aim to prescribe the value of  $\Gamma$  but check the results for several values.

Taking the absolute value of each term in Eq. (10), preserving the overall negative sign and using  $\Gamma_k = 2W_{0k}$ , we get the formula

$$\Delta E^{\text{QD2}} = - \sum_k \frac{|W_{0k}|^2}{\sqrt{(E_k - E_0)^2 + 4|W_{0k}|^2}}. \quad (11)$$

This was found to work properly in quasi-degenerate situations which can otherwise be handled by the substantially more complicated quasi-degenerate PT formalism [11]. We note that another type of straightforward modification of the MP2 formula was proposed by Assfeld et al. [44], who applied the unexpanded square root which occurs in the exact formula of the corresponding 2-by-2 problem for each state. As this expression does not contain energy denominators, it may also be useful in quasi-degenerate situations.

### NUMERICAL EXAMPLES

The efficiency of the above ideas has been tested calculating a few examples which are to be considered as forming a preliminary rather than representative set. Table I presents correlation energies for He and Ne atoms, the LiH molecule, and a cluster of 8 hydrogen atoms arranged in a linear chain with an equidistant (“metallic”) geometry of  $R = 1 \text{ \AA}$ . Second- and third-order (MP $n$ ) energies are evaluated with standard partitioning (denoted by MP $n$ -Koopmans in Table I), with the imaginary

**TABLE I**  
Second- and third-order correlation energies (a.u.) in various partitionings as compared to CISD and QCISD(T).

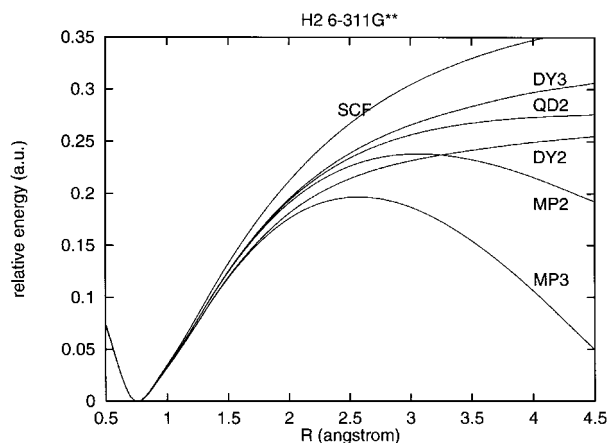
Method	He(TZ2P)	Ne(TZP)	LiH(6-31G**)	H <sub>8</sub> (6-31G**)
MP2-KOOPMANS	−0.029972	−0.227947	−0.035922	−0.132450
QD2	−0.029937	−0.227865	−0.035897	−0.132324
MP2-MP2	−0.030496	−0.243533	−0.037183	−0.145077
MP2-DYSON2	−0.030476	−0.242371	−0.037054	−0.142052
MP3-KOOPMANS	−0.035344	−0.227353	−0.037054	−0.157396
MP3-MP2	−0.035524	−0.225853	−0.043847	−0.161541
MP3-DYSON2	−0.035518	−0.226016	−0.043813	−0.160911
CISD	−0.036487	−0.224202	−0.045674	−0.158255
QCISD(T)		−0.231893		−0.168463

level shift introduced in Ref. [16] [QD2 of Eq. (11)], with real level shifts obtained both by MP2 [Eq. (9)] and by second-order Dyson correction [Eq. (6)] to the one-particle energies (MP $n$ -MP2 and MP $n$ -Dyson, respectively). Variational configuration interaction with singles and doubles (CISD) values are given for comparison, and for Ne and H<sub>8</sub> the QCISD(T) (T stands for triples) estimates are also indicated. We see that the small imaginary level shifts do not affect correlation energies appreciably, systems in Table I not being (quasi)degenerate. The applied real shifts are much larger. Values presented for He, Ne, and LiH give one a feeling that a pretty good improvement may be achieved by this repartitioning, although at the second-order standard MP-Koopmans values appear to be more balanced. This can be seen from the example of Ne where the MP2-Dyson and especially the MP2-MP2 repartitionings apparently exhibit an overcorrection. At third order, however, the improvement toward the variational values is remarkable in each case. The performance of the correction is especially advantageous for the H chain for which the gap-closing effect of the Dyson equation is well established.

It may be of interest to check not only absolute values but also chemical energy differences. In Table II we report the inversion barrier for ammonia where the effect of repartitioning is very small but mostly steps in the good direction. The improvement of the second- and third-order total energies is substantial. The second-order barrier in the Epstein–Nesbet (EN2) partitioning is also included in the table, and it seems to be the best among second-order results. This is not the case in general, however, upon checking the cis and trans barrier of peroxide, Dyson-corrected values proved to be rather bad and EN2 results were simply

**TABLE II**  
Second- and third-order total energies and inversion barrier (a.u.) of the NH<sub>3</sub> molecule in 6-311G\*\* basis set.

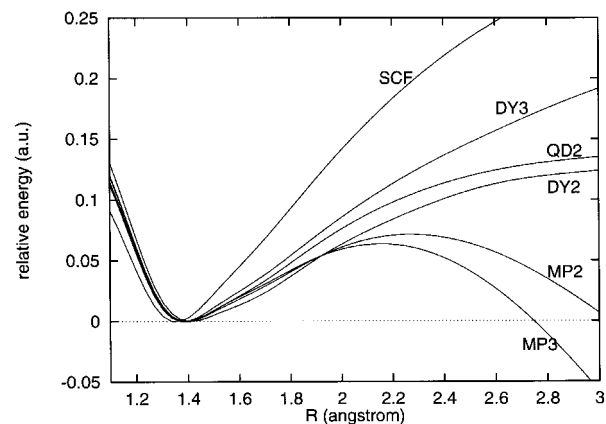
	Pyramidal	Planar	Barrier
SCF	-56.210397	-56.200814	0.009583
MP2	-56.427497	-56.417689	0.009808
QD2	-56.427428	-56.417598	0.009830
EN2	-56.480479	-56.470515	0.009964
DY2	-56.443469	-56.433693	0.009776
MP3	-56.439803	-56.429630	0.010173
DY3	-56.440335	-56.430095	0.010240
QCISD(T)	-56.447435	-56.437057	0.010378



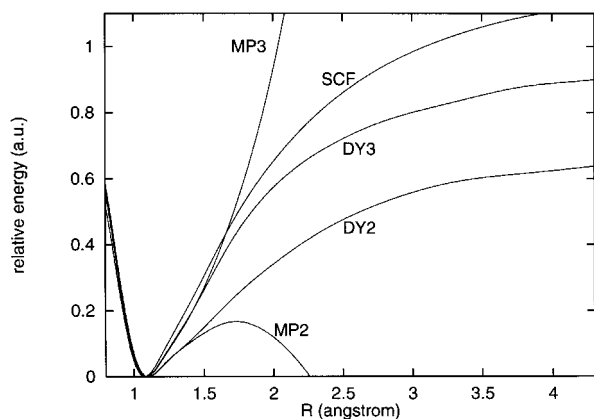
**FIGURE 2.** Potential curve of H<sub>2</sub> molecule in 6-311G\*\* basis set, obtained with imaginary (QD) and real level shift (DY2, DY3) technique. Closed-shell HF SCF and MP curves are shown for comparison.

pathological. The occasionally catastrophic behavior of the EN2 partitioning was also reported by other authors [45], though in other cases it was used successfully with multiconfigurational reference states [45–47].

Potential curves of H<sub>2</sub>, F<sub>2</sub>, and N<sub>2</sub> are presented in Figures 2–4 including large interatomic distances for which the single-reference MP $n$  corrections fail. We computed the curves also by second-order imaginary level shift technique [16] (denoted by QD2) which is designed for quasi-degenerate problems using  $\Gamma_k = 2W_{0k}$  as the damping constant. As reported in previous studies [16, 17, 42], the dissociation is described in a qualitatively correct manner by the QD2 approach in each case. It was interesting to us to realize that the Dyson-corrected level shifts may also result in



**FIGURE 3.** The same as Fig. 2, for the F<sub>2</sub> molecule.



**FIGURE 4.** Potential curve of  $N_2$  molecule in 6-311G\*\* basis set, using RHF-based perturbation theory with different partitionings; DY2 and DY3 indicates real denominator shift.

potential curves with a roughly acceptable dissociation behavior (DY2 and DY3 in Figs. 2–4) within the investigated range. The reason for this is that for large interatomic distances the second-order Dyson equation [Eq. (6)] does not tend to close the HOMO–LUMO gaps as it usually does at around equilibrium geometries, but conversely, it tends to remove quasi-degeneracies. This is equally seen for each case studied including  $N_2$  with multiple-bond dissociation. We do not claim, however, that this latter level shift technique can be used as a general and automatic tool for dissociation studies.

## APSG Reference State

### GROUND STATE

The use of Dyson- or MP2-corrected one-electron energies involves that, in some way, correlation effects are included already at the zeroth order. This can be done, however in a more systematic manner. Various attempts to use multireference (MR) PT [5–10] or MR coupled-cluster [12–14] approaches reflect the importance of this issue. Here we discuss the idea of using strongly orthogonal geminals to construct the zeroth order and evaluating perturbation corrections to this reference state. Such an approach has been initiated a long time ago [25, 26] and has been discussed recently for approximate geminals [27–30].

We define the ground-state wave function for a system of  $N$  (even) electrons as

$$\Psi_0^{\text{APSG}} = \psi_1^+ \psi_2^+ \dots \psi_{N/2}^+ |\text{vac}\rangle. \quad (12)$$

The strongly orthogonal geminals  $\psi_i^+$  are expanded as

$$\psi_i^+ = \sum_{\mu < \nu}^{(i)} C_{\mu\nu}^i a_\mu^+ a_\nu^+, \quad i = 1, 2, \dots, \frac{N}{2}, \quad (13)$$

where the superscript  $(i)$  on the summation indicates that only those indices  $\mu$  and  $\nu$  are considered which belong to the subspace assigned to geminal  $i$ . In Eq. (13) operators  $a_\mu^+$  ( $\mu \in i$ ) create electrons on orbitals spanning the  $i$ th subspace. The subspaces  $i$  can be built up by mutually exclusive sets of orthogonal one-electron functions which maintain strong orthogonality [48–50]. The expansion coefficients  $C_{\mu\nu}^i$  can be optimized variationally by solving a set of coupled local 2-electron Schrödinger equations [27, 30, 51] for each subspace. Optimization of the subspaces themselves leads to the so-called APSG wave function [48–50] which represents the variational minimum within the wave function class specified by Eq. (12). The APSG method is size-consistent and, being trivially exact for a two-electron system, it describes properly the single-bond dissociation. It does not give, however, a sufficiently large fraction of correlation energy which motivated the development of extended geminal schemes [52–56]. Here we discuss the possibility of using the APSG wave function as a reference state in MBPT.

Dealing with geminals in a many-body theory is easier if we study their algebraic properties. The commutators between creation/annihilation operators for the composite quasi-particles can be written as

$$[\psi_i^+, \psi_k^+] = [\psi_i^-, \psi_k^-] = 0, \quad (14)$$

$$[\psi_i^-, \psi_k^+] = \delta_{i,k} \hat{Q}_i, \quad (15)$$

where the quasiparticle commutator has the form [27, 30, 51, 57, 58]

$$\hat{Q}_i = 1 - \sum_{\mu\nu}^{(i)} P_{\nu\mu}^i a_\mu^+ a_\nu \quad (16)$$

with  $\mathbf{P}^i$  being the first-order density matrix for geminal  $i$ , for which, using the convention  $C_{\mu\lambda}^i = -C_{\lambda\mu}^i$  for  $\mu > \lambda$ , we get [30, 51, 57, 59]:

$$P_{\nu\mu}^i = \langle \psi_i | a_\mu^+ a_\nu | \psi_i \rangle = \sum_{\lambda}^{(i)} C_{\mu\lambda}^i C_{\nu\lambda}^i. \quad (17)$$

Relation (15), which is a consequence of the strong orthogonality of the geminals [57], is extremely important as it tells us that the quasi-particle creation and annihilation operators commute for different geminals. This permits us to use an analogous algebra in the evaluation of matrix elements as if we had a single-reference function.

The above equations are valid only if one considers a single geminal within each subspace. This is normally the ground-state solution of each two-electron problem. For the treatment of excited states and PT corrections one needs locally excited geminals as well:

$$\psi_{ia}^+ = \sum_{\mu < \nu}^{(i)} C_{\mu\nu}^{ia} a_{\mu}^+ a_{\nu}^+, \quad (18)$$

where  $a$  labels the excited state of the  $i$ th geminal. The algebraic properties are defined by the following quasi-particle commutator:

$$[\psi_{ja}^-, \psi_{ib}^+] = \delta_{ij} \hat{Q}_{ab}^i, \quad (19)$$

$$\hat{Q}_{ab}^i = \delta_{ab} - \sum_{\alpha\beta}^{(i)} P_{\alpha\beta}^{iab} a_{\alpha}^+ a_{\beta}. \quad (20)$$

(For the transition density matrix  $P^{iab}$ , see below.)

While the optimization of the expansion coefficients is a trivial and fast algorithm, finding the proper one-electron functions which span the subspaces is difficult and can be quite demanding computationally. This can be done by successive orbital rotations governed by the appropriate gradients  $g_{\mu\nu}$  used also for optimizing multiconfiguration self-consistent field (MCSCF) orbitals [60]:

$$g_{\mu\nu} = 2(F_{\mu\nu} - F_{\nu\mu}) \quad (21)$$

for the rotation of the geminal pair  $\mu, \nu$ , where  $\mathbf{F}$  is the generalized Fock matrix which, for geminals reads:

$$F_{\mu\nu} = \sum_{\lambda}^{(i)} h_{\mu\lambda} P_{\lambda\nu}^i + \sum_{\sigma\kappa\lambda}^{(i)} [\sigma\lambda|\kappa\mu] \Gamma_{\kappa\nu\sigma\lambda}^i + \sum_{\lambda}^{(k)} \sum_{j(\neq i)}^{(j)} [\sigma\lambda|\kappa\mu] \Gamma_{\kappa\nu\sigma\lambda}^{ji} \quad (22)$$

( $\mu \in k, \nu \in i, k \neq i$ ) in terms of spatial orbitals;  $\Gamma_{\kappa\nu\sigma\lambda}^i$  is the element of the second-order density matrix where  $\kappa, \nu, \sigma$ , and  $\lambda$  belong to the  $i$ th geminal. It takes the particularly simple form

$$\Gamma_{\kappa\nu\sigma\lambda}^i = 2C_{\kappa\nu}^i C_{\sigma\lambda}^i. \quad (23)$$

If  $\kappa$  belongs to the  $j$ th subspace and  $\nu$  to the  $i$ th, we get the following expression for the second-order density matrix:

$$\Gamma_{\kappa\nu\sigma\lambda}^{ji} = P_{\sigma\kappa}^j P_{\lambda\nu}^i - \frac{1}{2} P_{\lambda\kappa}^j P_{\sigma\nu}^i. \quad (24)$$

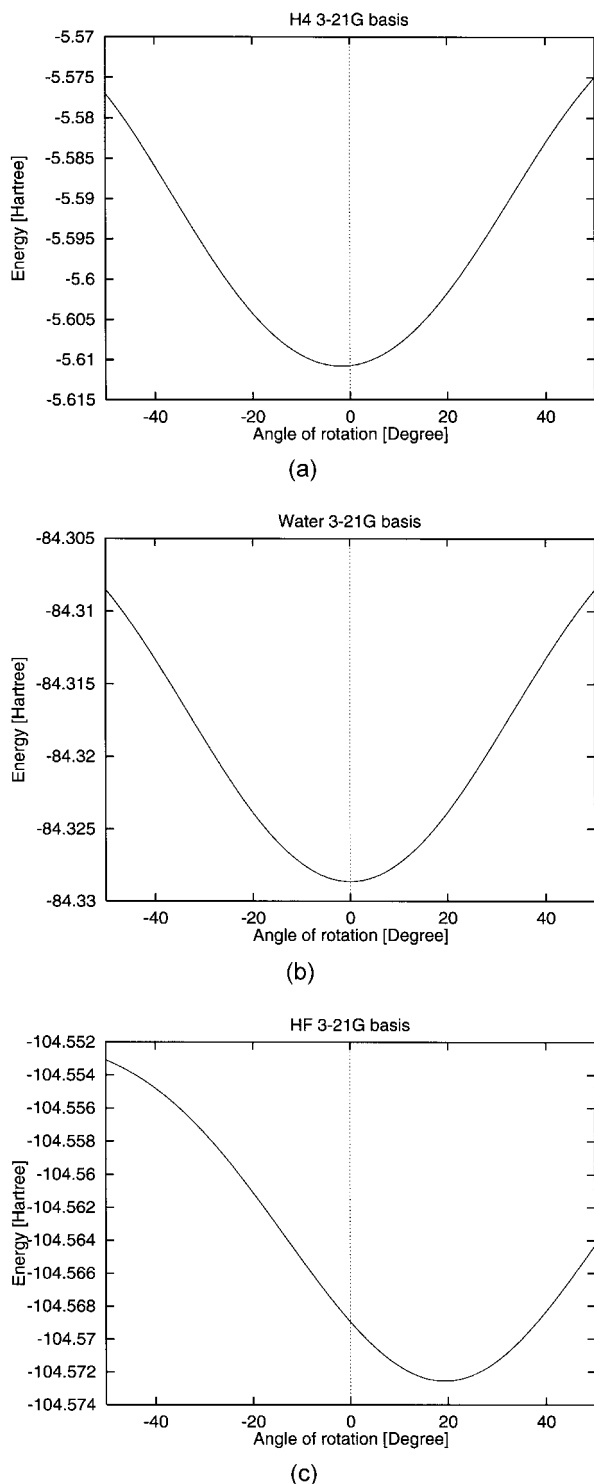
Note that the intrageminal contribution (23) factorizes to the product of geminal coefficients, while the intergeminal contribution (24) has the structure of the second-order density matrix of HF theory, thus using matrix  $\Gamma$  requires neither extra computations nor extra storage. The  $k \neq i$  restriction in Eq. (22) reflects that intrageminal orbital pairs need not be rotated during optimization as the two-electron problems are exactly solved within each subspace.

The convergence of such an optimization procedure may nevertheless be slow, so the selection of initial orbitals is of extreme importance. An example is provided by Table III where the total energy of the LiH molecule is shown at different levels. Although the basis is very small (minimal STO-6G), the subspace optimization is not trivial as shown by the second row of Table III. The corresponding energy was thought to be optimized if Ref. [61], but using Boys LMOs as initial guess one gets a better energy without any optimization. Varying the Boys orbitals one still gets an energy lowering of 0.05 mH. (The acronym SLG in Table III and below means strictly localized geminals, expressing that the geminals are not fully optimized but are expanded in arbitrarily selected orthogonal subspaces.)

The fact that Boys LMOs represent an appropriate initial guess can also be inferred from Figure 5. We plot there the variation of the total energy of some molecules as a function of a single selected orbital rotation parameter. The scale is chosen so that the Boys LMOs correspond to  $0^\circ$ . It is apparent that in two of the cases the variational minimum is

**TABLE III**  
Test calculations for LiH in STO-6G basis for comparison to another optimized APSG method (a.u.).

Method	Energy
HF	-7.96663
Optimized in Ref. [61]	-7.97981
SLG-Boys	-7.98085
Opt.-APSG	-7.98090



**FIGURE 5.** Variation of total energies as function of orbital rotation parameters near to SLG-Boys wave function (3-21G basis). (a)  $H_4$ , mixing the occupied bonding LMOs of the  $H_2$  molecules; (b)  $H_2O$ , mixing the lowest occupied bonding LMO of the O—H bonds; (c) HF, mixing the lowest occupied bonding LMO of the H—F bond and the lowest nonbonding LMO of F.

almost at  $0^\circ$ , while for the hydrogen fluoride it is at around  $20^\circ$ , but it is still closer to the Boys limit than, say, to the canonical MOs.

Having obtained the reference state, it may be useful for a subsequent perturbation treatment. The relevant second-order formulas have already been published in Refs. [27–29]. Among these, delocalization-type corrections due to single-electron transfers vanish if the orbitals are fully optimized, while one still can evaluate the second-order intergeminal dispersion energy:

$$\begin{aligned} \Delta E(\text{disp}) &= - \sum_{j < l} \sum_{ab}^{(M_S=0)} \frac{|[j_0 l_0 | j_a l_b] - \frac{1}{2} [j_0 l_0 | l_b j_a]|^2}{E_l^b + E_j^a - E_l^0 - E_j^0} \\ &\quad - \frac{1}{4} \sum_{j < l} \sum'_{ab} \frac{|[j_0 l_0 | j_a l_b]|^2}{E_l^b + E_j^a - E_l^0 - E_j^0}, \end{aligned} \quad (25)$$

where the prime means the restriction  $M_S^{a,b} = \pm 1$ ,  $M_S^a + M_S^b = 0$ ,  $j_a$  is the  $a$ th excited state of the  $j$ th geminal, and the transformed integrals over geminal labels can be expanded as

$$[j_0 l_0 | j_a l_b] = \sum_{\mu\nu}^{(j)} \sum_{\lambda\sigma}^{(l)} [\mu\lambda | \sigma\nu] P_{\mu\nu}^{j_0 a} P_{\lambda\sigma}^{l_0 b}. \quad (26)$$

The first-order transition density matrix element between the ground and  $a$ th state of the  $j$ th geminal reads as:

$$P_{\mu\nu}^{j_0 a} = \sum_{\lambda} (C_{\mu\lambda}^{j_0} C_{\nu\lambda}^{j a} + C_{\lambda\mu}^{j_0} C_{\lambda\nu}^{j a}). \quad (27)$$

Though the APSG wave function represents a highly correlated multiconfiguration reference state, derivation of this result is straightforward due to the simple algebraic rules of the composite-particle geminal operators [Eqs. (14)–(15)]. To arrive at Eq. (25), one defines the zero-order Hamiltonian in terms of ground- and excited-state geminals as

$$\hat{H}_0 = \sum_i \sum_a^{(i)} E_i^a \psi_{ia}^+ \psi_{ia}^-, \quad (28)$$

which has the property that the ground-state APSG wave function of Eq. (12) as well as similar wave functions in which one or more geminal is excited, are eigenfunctions of  $\hat{H}_0$ . The pairwise interaction of two such local excitations results in Eq. (25) by standard second-order Rayleigh-Schrödinger PT.



**TABLE IV**  
Energies of model systems (a.u.).

Basis	Method	H <sub>4</sub>	H <sub>2</sub> O	HF
STO-3G	HF	-1.652457	-74.964107	-98.572412
	SLG-Boys	-1.695297	-75.003767	-98.593229
	Opt.-APSG	-1.695760	-75.010899	-98.597985
	Opt.-APSG + disp2	-1.698419	-75.015881	-98.597985
	MP2	-1.686618	-75.004157	-98.590632
	CISD	-1.715532	-75.019737	-98.599827
3-21G	HF	-1.827905	-75.582739	-99.460219
	SLG-Boys	-1.873473	-75.613209	-99.488554
	Opt.-APSG	-1.875250	-75.648392	-99.515423
	Opt.-APSG + disp2	-1.879222	-75.688531	-99.572902
	MP2	-1.869325	-75.707172	-99.581585
	CISD	-1.889984	-75.710692	-99.582181

In Tables IV and V, a few numbers are given illustrating the effect of orbital optimization in very small basis sets. (We do not have yet numbers for larger molecules and/or larger bases.) The bond length of HF was optimized at the HF/3-21G level, while for the water molecule we used  $r(\text{OH}) = 1.01 \text{ \AA}$  and  $\alpha(\text{HOH}) = 104^\circ$ . The H<sub>4</sub> cluster was constructed in a distorted arrangement:  $r_{12} = r_{34} = 0.74 \text{ \AA}$ ,  $r_{23} = 1.0 \text{ \AA}$ ,  $\alpha(123) = 80^\circ$ ,  $\alpha(234) = 70^\circ$ , and the (1234) dihedral angle was  $20^\circ$ .

One can observe that in minimal basis the Boys localized orbitals represent a rather good initial guess to fully optimized ones, while in split-shell basis the optimization is more essential. It is also important that, with the exception of the H<sub>4</sub> system, the dispersion energies, collected separately in Table V, are quite sensitive to the optimization.

To judge the amount of correlation energy which can be described by the APSG + PT approach, one will need to see calculations in larger basis sets, at least of double  $\zeta$  polarized (DZP) quality. The small basis results of Table IV already indicate that the dispersive correction alone is not sufficient to reach the MP2 or CISD quality. At the APSG +

disp level, all local excitations have been accounted for, as well as the intrageminal single electron transfers which vanish upon optimization. However, delocalization of the geminals involving two electron transfers are missing from this approximation and may become important in larger systems and/or larger basis sets.

### EXCITED STATES

The APSG wave function may be a useful reference state for the calculation of electronically excited states, too [62]. In the Tamm–Dankoff approach (TDA) [63], essentially equivalent to the equation-of-motion (EOM) technique [60], one defines the excitation operator  $\hat{O}^+$  for the  $n$ th excited state  $|n\rangle$

$$\hat{O}_n^+|0\rangle = |n\rangle \quad (29)$$

and expands it as

$$\hat{O}_n^+ = \sum_K X_K^n \hat{A}_K^+ \quad (30)$$

**TABLE V**  
Dispersion contributions to the energy of model systems (a.u.).

Basis	Method	H <sub>4</sub>	H <sub>2</sub> O	HF
STO-3G	SLG-Boys	-0.002661	-0.005452	-0.000000
	Opt.-APSG	-0.002659	-0.004982	-0.000000
3-21G	SLG-Boys	-0.003917	-0.008690	-0.020686
	Opt.-APSG	-0.003972	-0.040139	-0.057479

For the expansion coefficients  $X_K^n$  the general TDA equations are written as

$$\sum_K \mathcal{A}_{LK} X_K^n = \omega_n \sum_K \mathcal{S}_{LK} X_K^n, \quad (31)$$

where  $\omega_n = E_n - E_0$  are the excitation energies and the TDA matrices are defined as

$$\begin{aligned} \mathcal{A}_{LK} &= \langle 0 | [\hat{A}_L^-, [\hat{H}, \hat{A}_K^+]] | 0 \rangle \\ &= \langle 0 | \hat{A}_L^- (\hat{H} - E_0) \hat{A}_K^+ | 0 \rangle \end{aligned} \quad (32)$$

and

$$\mathcal{S}_{LK} = \langle 0 | [\hat{A}_L^-, \hat{A}_K^+] | 0 \rangle. \quad (33)$$

We recall that the general TDA equations (31) are exact as far as the state  $|0\rangle$  is the true ground state and the operator expansion of Eq. (30) is complete. Substituting  $|0\rangle$  with the Hartree–Fock state and limiting the expansion to single excitations, one arrives at the CI with singles (CIS) scheme, a simple, popular but not very accurate approximation to the general TDA equations.

An important consistency requirement of the TDA equations is expressed by

$$\hat{O}_n^- |0\rangle = 0 \quad (34)$$

(the ground state cannot be deexcited). The CIS equations satisfy this requirement, but their improvement within TDA is not trivial as better reference states or larger operator manifolds may easily violate Eq. (34).

It may be interesting to investigate whether an APSG reference state could be useful for this goal. Formally, the answer is positive. Taking Eq. (12) as the approximation for the ground state, and defining the excitation operator manifold as

$$\hat{A}_K^+ = \psi_{pa}^+ \psi_{i0}^-, \quad (35)$$

where  $\psi_{i0}^-$  annihilates a ground-state geminal and  $\psi_{pa}^+$  creates one in the  $a$ th excited state, Eq. (34) remains valid and the APSG-TDA matrices become

$$\mathcal{A}_{LK} = \langle \Psi_0^{\text{APSG}} | \psi_{j_0}^+ \psi_{qa}^+ \hat{H} \psi_{pb}^+ \psi_{i_0}^- | \Psi_0^{\text{APSG}} \rangle - E_0 \mathcal{S}_{LK} \quad (36)$$

and

$$\mathcal{S}_{LK} = \langle \Psi_0^{\text{APSG}} | \psi_{j_0}^+ \psi_{qa}^- \psi_{pb}^+ \psi_{i_0}^- | \Psi_0^{\text{APSG}} \rangle. \quad (37)$$

It is to be mentioned that geminal-type wave functions may be useful not only in connection with TDA but also with the random-phase approximation (RPA). In particular, Öhrn and Linderberg have shown that the so-called antisymmetrized geminal power (APG) wave function, where each geminal is identical, serves as an appropriate reference state for RPA calculations [64, 65].

Evaluation of matrix elements in Eqs. (36) and (37) is lengthy but straightforward by the algebraic rules given earlier. For example, matrix  $\mathcal{S}$  is obtained as

$$\begin{aligned} \mathcal{S}_{LK} &= \delta_{ij} \delta_{pq} (\delta_{iq} \delta_{ab} + (1 - \delta_{iq}) \langle \hat{Q}_{ab}^q \rangle), \\ a, b \neq 0, L &= \{jq\}, K = \{ipb\}. \end{aligned} \quad (38)$$

The excitation space represented by Eq. (35) describes several types of single and double excitations (in terms of electrons); thus it may be more adequate to describe electronic excitations than the CIS scheme. However, intergeminal charge-transfer-type single-electron excitations are missing from Eq. (35)—they should be accounted for by a suitable perturbation of the TDA equations. We do not have yet any numerical results for excitation energies obtained by this scheme; work in both lines is now in progress.

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## References

1. P.-O. Löwdin, *Int. J. Quant. Chem.* **2**, 867 (1968).
2. P. S. Epstein, *Phys. Rev.* **28**, 695 (1926).
3. R. K. Nesbet, *Proc. Roy. Soc. (London)* **A230**, 312 (1955).
4. C. Møller and M. S. Plesset, *Phys. Rev.* **46**, 618 (1934).
5. S. Kucharski and R. Bartlett, *Int. Quant. Chem. S* **22**, 383 (1988).
6. K. Wolinski and P. Pulay, *J. Chem. Phys.* **90**, 3647 (1989).
7. R. Murphy and R. P. Messmer, *Chem. Phys. Lett.* **183**, 443 (1991).
8. W. Duch and G. H. Diercksen, *Phys. Rev. A* **46**, 95 (1992).
9. K. Andersson, P.-Å. Malmqvist, and B. O. Roos, *J. Chem. Phys.* **96**, 1218 (1992).
10. S. Zarrabian and J. Paldus, *Int. Quant. Chem.* **38**, 761 (1990).
11. I. Shavitt and L. T. Redmon, *J. Chem. Phys.* **73**, 5711 (1980).
12. X. Li and J. Paldus, *J. Chem. Phys.* **103**, 1024 (1995).
13. S. Berkovic and U. Kaldor, *J. Chem. Phys.* **98**, 3090 (1993).

14. P. G. Szalay and R. Bartlett, *J. Chem. Phys.* **103**, 3600 (1995).
15. X. Assfeld, J. L. Almlöf, and D. G. Truhlar, *Chem. Phys. Lett.* **241**, 438 (1995).
16. P. R. Surján and Á. Szabados, *J. Chem. Phys.* **104**, 3320 (1996).
17. P. R. Surján and Á. Szabados, *Acta Univ. Debreceniensis PC* **30**, 97 (1995).
18. D. Hegarty and M. A. Robb, *Mol. Phys.* **37**, 1455 (1979).
19. J. Mášik, I. Hubač, and P. Mach, *Int. J. Quant. Chem.* **53**, 207 (1995).
20. U. Kaldor, *Int. Quant. Chem.* **28**, 103 (1985).
21. E. Kapuy, F. Bartha, F. Bogár, and C. Kozmutza, *Theor. Chim. Acta* **72**, 337 (1987).
22. E. Kapuy, F. Bartha, C. Kozmutza, and F. Bogár, *J. Mol. Struct. (THEOCHEM)* **170**, 59 (1988).
23. E. Kapuy, F. Bartha, F. Bogár, Z. Csèpes, and C. Kozmutza, *Int. Quant. Chem.* **37**, 139 (1990).
24. S. Diner, J.-P. Malrieu, and P. Clavery, *Theor. Chim. Acta* **13**, 1, 18 (1969).
25. E. Kapuy, *Theor. Chim. Acta* **6**, 281 (1966).
26. E. Kapuy, *Theor. Chim. Acta* **12**, 397 (1968).
27. P. R. Surján, I. Mayer, and I. Lukovits, *Phys. Rev. A* **32**, 748 (1985).
28. P. R. Surján, *Int. J. Quant. Chem.* **52**, 563 (1994).
29. P. R. Surján, *Int. J. Quant. Chem.* **55**, 109 (1995).
30. P. R. Surján, in *Theoretical Models of Chemical Bonding*, Vol. 2, *The Concept of the Chemical Bond*, Z. B. Maksić (ed.) (Springer, Berlin-Heidelberg, 1990), p. 205.
31. P. R. Surján and Á. Szabados, to appear.
32. B. T. Pickup and O. Goscinski, *Mol. Phys.* **26**, 1013 (1973).
33. J. Öhrn and G. Born, *Adv. Quant. Chem.* **13**, 1 (1981).
34. J. Oddershede, in *Advances in Chemical Physics* (Wiley, New York, 1987), Vol. 69, p. 201.
35. W. Kutzelnigg and D. Mukherjee, *J. Chem. Phys.* **90**, 5578 (1989).
36. J. Palmer and J. Ladik, *J. Comput. Chem.* **15**, 814 (1994).
37. F. Bogar, W. Förner, E. Kapuy, and J. Ladik, *J. Mol. Struct. (THEOCHEM)* **391**, 193 (1997).
38. S. Suhai, *Phys. Rev. B* **27**, 3506 (1983).
39. S. Suhai, *Phys. Rev. B* **52**, 1674 (1995).
40. J. Sun and R. J. Bartlett, *J. Chem. Phys.* **104**, 8553 (1996).
41. P. R. Surján, Á. Szabados, F. Bogár, and J. Ladik, *Solid State Commun.* **103**, 639 (1997).
42. P. R. Surján and Á. Szabados, *J. Chem. Phys.* **107**, 5677 (1997).
43. N. Forsberg and P.-Å. Malmqvist, *Chem. Phys. Lett.* **274**, 196 (1997).
44. X. Assfeld, J. E. Almlöf, and D. G. Truhlar, *CPL* **241**, 438 (1995).
45. R. B. Murphy and R. P. Messmer, *J. Chem. Phys.* **97**, 4170 (1992).
46. A. O. Mitrushenkov and P. Palmieri, *Chem. Phys. Lett.* **278**, 285 (1997).
47. A. O. Mitrushenkov, *J. Chem. Phys.* **105**, 10487 (1996).
48. T. Arai, *J. Chem. Phys.* **33**, 95 (1960).
49. W. Kutzelnigg, *J. Chem. Phys.* **40**, 3640 (1964).
50. K. J. Miller and K. Ruedenberg, *J. Chem. Phys.* **48**, 3444 (1968).
51. P. R. Surján, *Phys. Rev. A* **30**, 43 (1984).
52. I. Røeggen, *J. Chem. Phys.* **79**, 5520 (1983).
53. I. Røeggen, *J. Chem. Phys.* **89**, 441 (1988).
54. I. Røeggen, *J. Chem. Phys.* **85**, 262 (1986).
55. I. Røeggen, *Mol. Phys.* **70**, 353 (1990).
56. P. Wind and I. Røeggen, *Chem. Phys.* **174**, 345 (1993).
57. P. R. Surján, *Croatica Chemica Acta* **62**, 579 (1989).
58. P. R. Surján *Second Quantized Approach to Quantum Chemistry* (Springer, Heidelberg, 1989).
59. C. Valdemoro, *Phys. Rev. A* **31**, 2114 (1985).
60. R. McWeeny, *Methods of Molecular Quantum Mechanics* (Academic, London, 1989).
61. S. Polezzo and P. Fantucci, *Mol. Phys.* **36**, 1835 (1978).
62. P. R. Surján, to appear.
63. D. J. Rowe, *Rev. Mod. Phys.* **40**, 153 (1968).
64. Y. Öhrn and J. Linderberg, *Int. J. Quant. Chem.* **12**, 161 (1977).
65. Y. Öhrn and J. Linderberg, *Int. Quant. Chem.* **15**, 343 (1979).