Partitioning Technique Procedure Revisited: Application to Many-Electron Systems Using the Møller–Plesset Hamiltonian

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ABSTRACT: A method to solve the electronic Schrödinger equation based on the modified partitioning procedure (MPP) and here denominated extended MPP (EMPP) is presented. We apply this procedure to molecular systems using the Møller–Plesset Hamiltonian. As we will show, it is possible with our approach to develop an optimization procedure to the electronic energy of many-electron systems. An advantage of the EMPP approach is that, in general, its results, with a minor number of configuration state functions, are better than various configuration interaction calculations with a larger number of configurations. Int J Quantum Chem 90: 1586–1595, 2002

Key words: partitioning technique; Møller–Plesset; CI; optimized atomic basis sets

1. Introduction

Many problems in quantum theory cannot be solved exactly. Except for some special cases, in which it is possible to solve the Schrödinger equation analytically—such as for a particle in the box, a harmonic oscillator, a rigid rotor, and the hydrogen atom—it becomes extremely complicated mainly for many-electron problems due to difficulty of separating the repulsion terms between electrons. In this context, in atomic and molecular problems the Hartree–Fock (HF) approximation is important as a starting point for more accurate procedures that include the effects of electron correlation as, for example, in cases of configuration interaction (CI) and many-body perturbation theory (MBPT). However, there are in the literature other methods that have not been sufficiently explored yet. One of these procedures is the so-called partitioning tech-

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nique (PT). During 1959–1965, Löwdin [1–3] was interested in the PT as a valuable procedure to determine the solution of eigenvalue problem

$$\hat{H}|\Psi_\ell\rangle = E_\ell|\Psi_\ell\rangle, \tag{1}$$

where

$$\hat{H} = \hat{H}_0 + \hat{V}$$

is the Hamiltonian operator. Löwdin's studies, however, were basically restricted to theoretical analysis to show the connection of the PT approach with the infinite-order perturbation theory and the interaction-variational methods [4]. In more recent years [5], the PT procedure has been used as a numerical tool for solving higher-order secular equations. Recently, one of us has shown [6, 7] that it is possible, by means of a new form of the PT equations, to determine the eigenvalues and eigenvectors of Eq. (1) explicitly. For this, the original development of the partitioning approach is modified in two aspects: (1) The partitioning technique is applied directly to auxiliary problem $\hat{H}_0|\ell\rangle = E_\ell^{(0)}|\ell\rangle$ instead of Eq. (1); (2) as reference ket it is used the eigenket $|\Psi_\ell\rangle$ of $\hat{H}$ instead of $|\ell\rangle$ eigenket of $\hat{H}_0$. As a consequence, differently from Löwdin's development [5], the reduced resolvent $\hat{R}$ in this new approach does not depend on $\hat{H}$ and we obtain a set of nonlinear algebraic equations for the wave operator matrix elements $W_{s\ell}$. Hence, we can determine E_ℓ directly in terms of $W_{s\ell}$ and the potential matrix elements $V_{s\ell}$. In this article, we apply this modified PT approach [modified partitioning procedure (MPP)] to molecular systems using the Møller–Plesset Hamiltonian and develop a procedure we call the extended MPP (EMPP), through which we can optimize the electronic energy of systems. The article is organized as follows: In Section 2, we present a summary of the MPP and obtain the fundamental equations to determine the eigenvalues and eigenvectors of $\hat{H}$. In Sections 3–5, we consider the many-electron problems. Specifically, we discuss basis sets and apply the MPP and EMPP to LiH, Li_2, BH, NH, HF, LiF, CO, N_2, BF, and F_2 systems. In these sections, the MPP and EMPP equations are also presented. Section 6 contains an analysis of the results and Section 7 our concluding remarks.

2. Modified Partitioning Procedure

We assume that the eigenvalues and eigenvectors of $\hat{H}_0$ are known. It is not necessary that $\hat{V}$ in $\hat{H} = \hat{H}_0 + \hat{V}$ be small. In the following, we would like to determine the eigenvalues and eigenstates of $\hat{H}$. In the usual notation, the auxiliary problem is

$$\hat{H}_0|\ell\rangle = E_\ell^{(0)}|\ell\rangle, \qquad \ell = 0, 1, \ldots \tag{2}$$

and the principal problem is to solve

$$\hat{H}|\Psi_\ell\rangle = E_\ell|\Psi_\ell\rangle, \qquad \ell = 0, 1, \ldots \tag{3}$$

Now, we introduce the projection operator $\hat{Q}$ out of $|\Psi_\ell\rangle$

$$\hat{Q} \equiv \frac{|\Psi_\ell\rangle\langle\Psi_\ell|}{C}, \tag{4}$$

and let $\hat{P}$ be its complement

$$\hat{P} = \hat{1} - \hat{Q}, \tag{5}$$

with

$$C = \langle\Psi_\ell|\Psi_\ell\rangle, \tag{6}$$

and the intermediate normalization condition

$$\langle\ell|\Psi_\ell\rangle = 1 \tag{7}$$

satisfied.

Operators $\hat{Q}$ and $\hat{P}$ correspond to the projection operators introduced by Löwdin [2], but here the reference ket that defines $\hat{Q}$ and $\hat{P}$ is not normalized. An analysis of Löwdin's development shows that the partitioning technique procedure is valid for any $\hat{H}$ subjected to the condition that $\hat{H}$ is a self-adjoint operator and describes a bound state; in particular, it is valid for $\hat{H}_0$. In this case, the fundamental operators in the theory are the reduced resolvent $\hat{R}$ defined by

$$\hat{R} \equiv \hat{P}(\hat{1}E_\ell^{(0)} - \hat{P}\hat{H}_0\hat{P})^{-1}\hat{P}, \tag{8}$$

and the operator $\hat{\Omega}$ given by

$$\hat{\Omega} \equiv (\hat{1} + \hat{R}\hat{H}_0)\hat{Q}, \tag{9}$$

where $\hat{R}$ is the resolvent operator of the electronic Schrödinger equation of the auxiliary problem (2). It differs from the operator obtained by Löwdin [2] because it contains $E_\ell^{(0)}$ and $\hat{H}_0$ instead of E_ℓ and $\hat{H}$, respectively, and $\hat{P}$ is defined in terms of $|\Psi_\ell\rangle$, while in Löwdin's development it is defined by $|\ell\rangle$. Therefore,

$\hat{\Omega}$ is an operator that also differs from the correspondent operator found by Löwdin because it contains $\hat{H}_0$ instead of $\hat{H}$ and $\hat{Q}$ is defined in terms of $|\Psi_\ell\rangle$. These differences have useful consequences in the applications [see Eqs. (18)–(21) below]. Similarly to Löwdin's development, it is possible to show that $\hat{H}_0\hat{\Omega} = E^{(0)}\hat{\Omega}$ under a certain condition. In fact, we have

$$(\hat{H}_0 - E^{(0)})\hat{\Omega} = (\hat{P} + \hat{Q})(\hat{H}_0 - E^{(0)})\hat{\Omega}. \quad (10)$$

Hence, using proprieties of $\hat{P}$, $\hat{Q}$ and $\hat{\Omega}$, if the condition

$$\hat{Q}E^{(0)}\hat{Q} = \hat{Q}(\hat{H}_0 + \hat{H}_0\hat{R}\hat{H}_0)\hat{Q} \quad (11)$$

is satisfied, we have

$$(\hat{H}_0 - E^{(0)})\hat{\Omega} = 0. \quad (12)$$

Substituting expression (8) into Eq. (11) and using (4), we find

$$|\ell\rangle = \hat{\Omega}\,\frac{|\Psi_\ell\rangle}{C}. \quad (13)$$

As $\hat{P}\hat{Q} = 0$, then $\hat{R}\hat{Q} = 0$, from which results that $\hat{R}\hat{H}_0\hat{Q} = -\hat{R}\hat{V}\hat{Q}$ (note that from $\hat{H}\hat{Q} = E_\ell\hat{Q}$ it follows: $\hat{R}\hat{H}\hat{Q} = 0$ and hence $\hat{R}\hat{H}_0\hat{Q} = -\hat{R}\hat{V}\hat{Q}$). Consequently, $\hat{\Omega}$ can be written as

$$\hat{\Omega} = (\hat{1} - \hat{R}\hat{V})\hat{Q}. \quad (14)$$

From Eqs. (13) and (14), we define a modified wave operator $\hat{W}$ as

$$\hat{W} \equiv C(\hat{1} - \hat{R}\hat{V})^{-1} \quad (15)$$

or

$$\hat{W} = \hat{1}C + \hat{R}\hat{V}\hat{W}. \quad (16)$$

Hence, from (13), (14), and (15), we obtain

$$|\Psi_\ell\rangle = \hat{W}|\ell\rangle. \quad (17)$$

In other words, $\hat{W}$ is such that when it acts on the known eigenvector $|\ell\rangle$ one obtains the eigenvector of interest $|\Psi_\ell\rangle$ of Eq. (1).

To apply Eq. (17), we consider an orthonormal complete set of eigenkets of $\hat{H}_0$, $\{|k\rangle, k = 0, 1, \ldots\}$. Hence, using (16) and the completeness relation $\sum_k |k\rangle\langle k| = \hat{1}$, we obtain

$$W_{s\ell} = C\delta_{s\ell} + \sum_{j,k} R_{sj}V_{jk}W_{k\ell}, \quad (18)$$

where $R_{sj} = \langle s|\hat{R}|j\rangle$, $V_{jk} = \langle j|\hat{V}|k\rangle$, and $W_{k\ell} = \langle k|\hat{W}|\ell\rangle$. In this notation, ℓ is fixed and $s = 0, 1, \ldots$. In view of Eq. (18), the matrix elements $W_{s\ell}$ are not fully determined because we still do not have the elements R_{sj} of the resolvent $\hat{R}$. They are obtained through the identity

$$(\hat{1}E_\ell^{(0)} - \hat{P}\hat{H}_0\hat{P})(\hat{1}E_\ell^{(0)} - \hat{P}\hat{H}_0\hat{P})^{-1} = \hat{1},$$

the relationships (4) and (5), and the expression

$$\langle\ell|\hat{H}_0\hat{R} = C\langle\ell| - \langle\Psi_\ell|, \quad (19)$$

obtained from (13). It follows, after some algebraic manipulation (see Appendix B), that

$$(E_\ell^{(0)} - E_s^{(0)})R_{sj} = \delta_{sj} - W_{s\ell}\delta_{\ell j}. \quad (20)$$

Therefore, substituting (20) into (18) for $s \neq \ell$, we obtain

$$(E_\ell^{(0)} - E_s^{(0)})W_{s\ell} - \sum_k (V_{sk} - W_{s\ell}V_{\ell k})W_{k\ell} = 0,$$
$$k, s = 0, 1, \ldots (s \neq \ell), \quad (21)$$

with [see (7) and (17)]

$$W_{\ell\ell} = 1. \quad (22)$$

With the matrix elements $W_{s\ell}$ obtained from (21), we can write $|\Psi_\ell\rangle$ and E_ℓ using (17) (note that $E_\ell = \langle\Psi_\ell|\hat{H}_0 + \hat{V}|\ell\rangle = E_\ell^{(0)} + \langle\ell|\hat{V}\hat{W}|\ell\rangle$). In fact, if we consider a subset of N eigenkets of $\hat{H}_0$ the set of Eqs. (21) and (22) is a nonlinear algebraic system for $W_{s\ell}$ with N equations and N unknown $W_{s\ell}$, whose solution is given for

$$|\Psi_\ell\rangle = \sum_k W_{k\ell}|k\rangle, \quad (23)$$

$$E_\ell = E_\ell^{(0)} + \sum_k V_{\ell k}W_{k\ell}, \quad (24)$$

which is the explicit solution of Eq. (1). In this article, the system of nonlinear equations has been solved with Brown's algorithm [8]. This algorithm solves a

TABLE I
LiH molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−7.9807468540	0.9826706486	−7.9893663622
86	$S-D$	−7.9992894548	0.9823435936	−8.0082391018
246	$S-T$	−7.9992969153	0.9823434620	−8.0082466963
418	$S-Q_4$	−7.9992986321	0.9823434317	−8.0082484440

Experimental, −8.0703 a.u. [15]; *equilibrium bond length*, 3.015 a.u. [16].

system of N nonlinear equations in N unknown variables. The method is based on an iterative procedure that is a variation of Newton's method using Gaussian elimination in a similar manner to the Gauss–Seidel process, with quadratic convergence. Concluding this section, we note that (21), (22), (23), and (24) are the fundamental equations of the MPP. From these equations it follows that our procedure is valid for any potential $\hat{V}$ (small or large), whose elements $V_{\ell k}$ exist. Hence, it can be applied to many-electron atomic and molecular systems.

3. Application to Many-Electron Systems

To apply the MPP to many-electron problems, we consider LiH, Li_2, BH, NH, HF, LiF, CO, N_2, BF, and F_2 systems and the Møller–Plesset Hamiltonian [9]. In this case, the Hamiltonian operator $\hat{H}_0$ will be defined by

$$\hat{H}_0 = \sum_i \hat{F}(i), \tag{25}$$

where $\hat{F}(i)$ is the Fock operator, given (in usual notation) by

$$\hat{F}(i) = \hat{h}(i) + \sum_j \{\hat{J}_j(i) - \hat{K}_j(i)\}. \tag{26}$$

For the potential $\hat{V}$, we have

$$\hat{V} = \hat{H} - \hat{H}_0 = \sum_i \left\{\hat{h}(i) + \sum_{j>i} \frac{1}{r_{ij}} - \hat{F}(i)\right\}$$

or

$$\hat{V} = \sum_i \left\{\sum_{j>i} \frac{1}{r_{ij}} - \sum_j \{\hat{J}_j(i) - \hat{K}_j(i)\}\right\}. \tag{27}$$

To apply Eqs. (21) and (22), it is necessary to choose a basis set $\{|k\rangle\}$ to determine the matrix elements $V_{s\ell}$. In this context, there are two possibilities: In Section 4, we consider the case where the basis set $\{|k\rangle\}$ is composed by the eigenfunctions of $\hat{H}_0$ and in Section 5 we take for $\{|k\rangle\}$ a basis set whose elements depend on an arbitrary parameter to be determined by a variational procedure.

4. MPP With Basis Set of $\hat{H}_0$

A usual basis set for many-electron calculations is formed by Slater determinants that are eigenfunc-

TABLE II
Li_2 molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−14.8680656776	0.9837757308	−14.8821481949
97	$S-D$	−14.8788590814	0.9836736781	−14.8931201708
360	$S-T$	−14.8788605277	0.9836736644	−14.8931216412
858	$S-Q_4$	−14.8788610640	0.9836736593	−14.8931221863
1236	$S-Q_5$	−14.8788610640	0.9836736593	−14.8931221863
1378	$S-S_6$	−14.8788610640	0.9836736593	−14.8931221863

Experimental, −14.9944 a.u. [15]; *equilibrium bond length*, 5.051 a.u. [16].

TABLE III
BH molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−25.1133952951	0.9877538256	−25.1265931780
133	$S - D$	−25.1715988609	0.9874202431	−25.1855283040
561	$S - T$	−25.1723535334	0.9874159177	−25.1862925928
1455	$S - Q_4$	−25.1740141708	0.9874063999	−25.1879744022
2247	$S - Q_5$	−25.1740148562	0.9874063960	−25.1879750963
2575	$S - S_6$	−25.1740150341	0.9874063950	−25.1879752765

Experimental, −25.273 a.u. [15]; *equilibrium bond length*, 2.336 a.u. [16].

tions of $\hat{H}_0 = \sum_i \hat{F}(i)$. Here, we consider this basis set. It is composed with Hartree–Fock–Roothaan reference function $|\phi_0\rangle$, and configuration state functions (CSFs) $\{|\phi_\ell\rangle\}$ obtained from $|\phi_0\rangle = |\chi_1\chi_2\ldots\chi_a\chi_b\ldots\chi_N\rangle$, by excitations to virtual molecular spin–orbitals (MSOs) $\chi_r, \chi_s, \ldots$. In this basis set, we have for matrix elements of $\hat{V}$

$$V_{\ell k} = \langle\phi_\ell|\hat{V}|\phi_k\rangle = \langle\ldots\chi_a\chi_b\ldots|\hat{V}|\ldots\chi_r\chi_s\ldots\rangle.$$

And, by the Condon–Slater rules [10, 11], we obtain

$$V_{\ell k} = \begin{cases} = -\dfrac{1}{2}\sum\limits_{i,j}\langle\chi_i\chi_j\|\chi_i\chi_j\rangle & \text{if the determinants } |\phi_\ell\rangle \text{ and } |\phi_k\rangle \text{ are identical } (a = r \text{ and } b = s) \\ = \langle\chi_a\chi_b\|\chi_r\chi_s\rangle & \text{if the determinants differ by two MSOs } (a \neq r \text{ and } b \neq s) \\ = 0 & \text{in the other cases,} \end{cases}$$

where $\langle\chi_i\chi_j\|\chi_i\chi_j\rangle$ is the usual notation for an antisymmetrized two-electron integral, equal to $\langle\chi_i\chi_j|\chi_i\chi_j\rangle - \langle\chi_i\chi_j|\chi_j\chi_i\rangle$.

The results for the ground state of LiH, Li_2, BH, NH, HF, LiF, CO, N_2, BF, and F_2 systems are presented in Tables I–X for several MPP basis sets $\{|k\rangle\}$ and compared to CI calculations with the same basis set. We note that our results agree with the CI results in all cases.

5. MPP With a General Basis Set

The fundamental equations of the MPP can be used with an arbitrary basis set $\{|k\rangle\}$. In particular, we can consider for $\{|k\rangle\}$ a basis set composed from atomic orbitals (AOs) that depend on a variational parameter γ. We will call such a formulation EMPP and show that the EMPP is an optimization process to the electronic energy. In fact, it is this aspect of the approach that has augmented our interest in developing the MPP because a limited configuration interaction can give results that are better that various CI calculations with a larger number of configurations (e.g., see Tables I and III–V). For this, we remember that in the atomic Gaussian functions we have for exponents the expression $-\alpha r_i^2$. Then,

TABLE IV
NH molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−54.8488173383	0.9906733487	−54.8655336256
75	$S - D$	−54.9069568851	0.9905210699	−54.9242250356
287	$S - T$	−54.9119972471	0.9905078681	−54.9293136659
747	$S - Q_4$	−54.9169194336	0.9904949758	−54.9342830546
1166	$S - Q_5$	−54.9169855568	0.9904948026	−54.9343498123
1385	$S - S_6$	−54.9169955515	0.9904947764	−54.9343599029
1429	$S - S_7$	−54.9169955535	0.9904947764	−54.9343599049
1436	$S - O$	−54.9169955537	0.9904947764	−54.9343599051

Experimental, −55.252 a.u. [17]; *equilibrium bond length*, 1.9614 a.u. [17].

TABLE V
HF molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−100.0218947997	0.9926522720	−100.0409092529
78	$S - D$	−100.1059072605	0.9925323727	−100.1255486955
298	$S - T$	−100.1067029401	0.9925312372	−100.1263503621
751	$S - Q_4$	−100.1088256690	0.9925282077	−100.1284890677
1163	$S - Q_5$	−100.1089101927	0.9925280870	−100.1285742277
1380	$S - S_6$	−100.1089174070	0.9925280768	−100.1285814963
1428	$S - S_7$	−100.1089176378	0.9925280764	−100.1285817289
1436	$S - O$	−100.1089176379	0.9925280764	−100.1285817289

Experimental, −100.527 a.u. [15]; *equilibrium bond length*, 1.733 a.u. [16].

we introduce a variational parameter γ as $-(\alpha/\gamma^2)\, r_i^2$, which can be written as

$$-\alpha\frac{\vec{r}_i}{\gamma}\cdot\frac{\vec{r}_i}{\gamma} = -\alpha\vec{r}_i'\cdot\vec{r}_i', \tag{28}$$

with $\vec{r}_i'=\vec{r}_i/\gamma$. In this case, we have

$$E_\ell = \langle\Psi_\ell'|\hat{H}|\Psi_\ell'\rangle, \tag{29}$$

where we write $|\Psi_\ell'\rangle$ to indicate that the wave function depends on γ, that is, the atomic Gaussian functions in $|\Psi_\ell'\rangle$ depend on electronic coordinates as $-\alpha r_i'^2$. A mathematical development shows that the parameterized energy $E_\ell(\gamma)$ can be written as

$$E_\ell(\gamma) = \langle\Psi_\ell'|\hat{H}'|\Psi_\ell'\rangle, \tag{30}$$

with

$$\hat{H}' = \sum_i\left\{-\frac{1}{2\gamma^2}\nabla_i'^2 - \sum_A\frac{Z_A}{|\gamma\vec{r}_i' - \vec{R}_A|} + \sum_{j>i}\frac{1}{|\gamma\vec{r}_i' - \gamma\vec{r}_j'|}\right\}, \tag{31}$$

where $\nabla_i'^2$ denotes the Laplacian in the variable $\vec{r}_i'$. We note that for $\gamma = 1$, $E_\ell\,(\gamma = 1) = E_\ell = \langle\Psi_\ell|\hat{H}|\Psi_\ell\rangle$.

Now we can replace, without generality loss, $\vec{r}_i'$ by $\vec{r}_i$ in $\hat{H}'$ and $|\Psi_\ell'\rangle$ and note that

$$\hat{H}' = \frac{1}{\gamma^2}\hat{T}_e + \hat{V}_{Ne}'(\gamma) + \frac{1}{\gamma}\hat{V}_e, \tag{32}$$

where $\hat{T}_e$ is the kinetic energy operator of the electrons for $\gamma = 1$, $\hat{V}_e$ is the electronic repulsive potential operator for $\gamma = 1$, and

$$\hat{V}_{Ne}'(\gamma) = -\sum_{iA}\frac{Z_A}{|\gamma\vec{r}_i' - \vec{R}_A|} \tag{33}$$

TABLE VI
LiF molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−106.9542217784	0.9878079573	−107.0117294363
111	S–D	−106.9544485936	0.9878076616	−107.0119590510
501	S–T	−106.9544531704	0.9878076556	−107.0119636843
1479	S–Q_4	−106.9544531884	0.9878076556	−107.0119636025
2649	S–Q_5	−106.9544531884	0.9878076556	−107.0119637025
3429	S–S_6	−106.9544531884	0.9878076556	−107.0119636025
3659	S–S_7	−106.9544531884	0.9878076556	−107.0119637025
3700	S–O	−106.9544531884	0.9878076556	−107.0119637025

Experimental, −107.502 a.u. [15]; equilibrum bond length, 2.8535 a.u. [16].

TABLE VII
CO molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−112.6848351562	0.9733710155	−112.9893752392
81	$S - D$	−112.7341415581	0.9733124849	−113.0400320634
310	$S - T$	−112.7373165600	0.9733087159	−113.0432941278
813	$S - Q_4$	−112.7378138944	0.9733081255	−113.0438051010
1213	$S - Q_5$	−112.7378372637	0.9733080978	−113.0438291110
1378	$S - S_6$	−112.7378376116	0.9733080974	−113.0438294685

Experimental, −113.377 a.u. [15]; *equilibrium bond length,* 2.1318 a.u. [16].

is the Coulombian attractive potential between electrons and nuclei in terms of the parameter γ. We remember that in MPP the Møller–Plesset Hamiltonian $\hat{H}_0$ for molecular systems is given by (25), i.e.,

$$\hat{H}_0 = \sum_i \left\{ -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \sum_j [\hat{J}_j(i) - \hat{K}_j(i)] \right\}$$
$$= \hat{T}_e + \hat{V}_{Ne} + \hat{\upsilon}^{\mathrm{HF}},$$

where $\hat{\upsilon}^{\mathrm{HF}}$ is the effective one-electron potential operator called HF potential and the operator $\hat{V}$ of Eq. (27) can be rewritten as

$$\hat{V} = \sum_i \left\{ \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_j [\hat{J}_j(i) - \hat{K}_j(i)] \right\}$$
$$= \hat{V}_e - \hat{\upsilon}^{\mathrm{HF}}. \tag{34}$$

Hence, the electronic functional obtained from MPP is

$$E_\ell = \langle \Psi_\ell | \hat{H} | \Psi_\ell \rangle$$
$$= E_\ell^{(0)} + \sum_k V_{\ell k} W_{k\ell}$$
$$= \langle \ell | \hat{T}_e | \ell \rangle + \langle \ell | \hat{V}_{Ne} | \ell \rangle + \sum_k \langle \ell | \hat{V}_e - \hat{\upsilon}^{\mathrm{HF}} \delta_{k\ell} | k \rangle. \tag{35}$$

Then, performing in (35) the necessary mathematical steps to introduce the transformation (28), it follows from Eqs. (30)–(33) that

$$E_\ell(\gamma) = \frac{1}{\gamma^2} \langle \ell | \hat{T}_e | \ell \rangle + \langle \ell | \hat{V}'_{Ne}(\gamma) | \ell \rangle + \frac{1}{\gamma} \sum_k W_{k\ell} \langle \ell | \hat{V} - \hat{\upsilon}^{\mathrm{HE}} \delta_{k\ell} | k \rangle. \tag{36}$$

Equation (36) is the γ-parameterized functional. The first and second variations relative to parameter γ in $E_\ell(\gamma)$ give the extreme condition and its respective classification. In fact, from Eq. (36) the condition

$$\frac{\partial E_\ell(\gamma)}{\partial \gamma} = 0 \tag{37}$$

gives

TABLE VIII
N_2 molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−108.8781363898	0.9711235381	−109.2266689781
81	$S - D$	−108.9541114491	0.9710307133	−109.3049069032
310	$S - T$	−108.9552637513	0.9710293054	−109.3060935834
813	$S - Q_4$	−108.9578747128	0.9710261154	−109.3087824475
1213	$S - Q_5$	−108.9578853931	0.9710261023	−109.3087934465
1378	$S - S_6$	−108.9578864353	0.9710261010	−109.3087945198

Experimental, −109.586 a.u. [15]; *equilibrium bond length,* 2.073 a.u. [16].

TABLE IX
BF molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−124.0810197206	0.9795286204	−124.2748212479
81	$S - D$	−124.0988769803	0.9795090242	−124.2930518928
310	$S - T$	−124.0993883276	0.9795084631	−124.2935739374
813	$S - Q_4$	−124.0994669009	0.9795083768	−124.2936541544
1213	$S - Q_5$	−124.0994675475	0.9795083761	−124.2936548146
1378	$S - S_6$	−124.0994675531	0.9795083761	−124.2936548203

Experimental, −124.777 a.u. [15]; *equilibrium bond length*, 2.3848 a.u. [16].

$$2\langle \ell|\hat{T}_e|\ell\rangle - \gamma^3\left\langle \ell\left|\frac{\partial}{\partial\gamma}\hat{V}'_{Ne}(\gamma)\right|\ell\right\rangle + \gamma\sum_k W_{k\ell}\langle \ell|\hat{V} - \hat{v}^{\mathrm{HF}}\delta_{k\ell}|k\rangle = 0. \quad (38)$$

One way of solving Eq. (38) is to use a self-consistent process in the integral that involves the operator $(\partial/\partial\gamma)\,\hat{V}'_{Ne}$. Another form is to expand this operator in a Taylor power series (developed in Appendix A) about $\gamma = 1$ and consider only the first-order terms, for example. Then, we obtain

$$\hat{V}'_{Ne}(\gamma) = (2-\gamma)\hat{V}_{Ne}.$$

And, Eq. (38) becomes

$$\gamma^3\langle \ell|\hat{V}_{Ne}|\ell\rangle + \gamma\sum_k W_{k\ell}\langle \ell|\hat{V} - \hat{v}^{\mathrm{HF}}\delta_{k\ell}|k\rangle + 2\langle \ell|\hat{T}_e|\ell\rangle = 0. \quad (39)$$

Here, the process consists of the following steps: (1) After solving the system of Eqs. (21)–(22), obtaining unknowns $W_{s\ell}$s, we determine the parameter γ using Eq. (39); (2) from Eq. (36) we find the optimized electronic energy. A fact to note is that

$$\frac{\partial^2 E_\ell(\gamma)}{\partial\gamma^2} > 0,$$

i.e., the parameter γ obtained from (39) gives a minimum value for $E_\ell(\gamma)$.

6. Results

In Tables I–X, we present the results obtained for LiH, Li_2, BH, NH, HF, LiF, CO, N_2, BF, and F_2 systems using the CI, MPP, and EMPP approaches with double-zeta valence (DZV) basis set [12, 13]. All calculations were carried out using the GAMESS software package [14] with the modifications we introduced to implement equations of MPP and EMPP. In Tables I–X, we have the ground-state energy and also the value of γ obtained for each case; the notation $S - T$, for example, means that the calculations have been performed with single, double, and triple excitations. From Eq. (28), the parameter γ modifies the exponents of basis set used; so, the EMPP allows us to define an atomic basis set that is good for the atom in that particular molecule. An analysis of the results shows some important facts. For example, for

TABLE X
F_2 molecule.

CSFs	Type	CI and MPM energy (a.u.)	γ	EMPP energy (a.u.)
1	Ref.	−198.7075347784	0.9793584644	−199.0244658394
86	$S - D$	−198.7933972619	0.9792998760	−199.1121406336
246	$S - T$	−198.7934503352	0.9792998398	−199.1121948288
418	$S - Q_4$	−198.7934923465	0.9792998111	−199.1122377281

Experimental, −199.670 a.u. [15]; *equilibrium bond length*, 2.679 a.u. [16].

systems Li_2, CO, N_2, LiF, BF, and F_2 an EMPP calculation with the reference function $|\phi_0'\rangle$ only (in $|\phi_0'\rangle$ the atomic basis set is modified by the inclusion of the parameter γ) gives a better result than a CI with the original atomic basis set. A similar result is verified for systems LiH, BH, NH, and HF when we compare the value for ground-state energy obtained by a CI in the original basis set and the results from EMPP with mono- and double excitations only but using the modified atomic γ basis set. In the results, the basis of CSFs for systems LiH and BH correspond to a full CI while for the others to a truncated CI. So, our results indicate that EMPP can be used with two finalities: to reduce the number of CSFs in the determination of correlated electronic energy and determine Gaussian exponents for the atomic basis set considering the atom in molecules.

TABLE XI
MP(2) energies.

Molecule	MP2 energy (a.u.)
LiH	−7.9807
Li_2	−14.8832
BH	−25.1495
NH	−54.9165
HF	−100.1421
LiF	−107.0827
CO	−112.8877
N_2	−109.1063
BF	−124.2379
F_2	−198.9556

7. Summary

In this article we presented a procedure to solve the electronic Schrödinger equation for molecular systems based on the partitioning technique of Hilbert space of the problem. This approach is a generalization of the Löwdin technique, which allows us to introduce a variational parameter out of which we can optimize the electronic energy of a particular state of the studied systems.

A characteristic of the MPP is that it has no dependence on the particular form of the Hamiltonian $\hat{H}$ ($\hat{H}_0 + \hat{V}$), i.e., the $\hat{V}$ potential in $\hat{H}$ may be small or large. Besides, the MPP does not present problems of convergence, typical of perturbation theory. Another characteristic of this approach is that all the results of the MPP reproduce the CI calculations for the same configuration space functions, as shown in Tables I–X. The MPP, however, does not use any matrix diagonilization process and allows us to introduce easily an optimization procedure (EMPP) to electronic energy and the basis set used. The results obtained through the EMPP in all cases are better than the corresponding CI calculations for the original LCAO basis set. Except for systems LiF and HF, the results obtained by means of the EMPP are better than the corresponding perturbation calculations, until second order, according to Table XI. We remark that in some cases the EMPP calculations, using only the HF reference, are already better than various CI calculations. In conclusion, our results indicate that the EMPP can be used to reduce the number of configurations in a CI calculation, optimize Gaussian basis sets, and, more important, correct CI results *a posteriori* to minimize the error arising from an inadequate LCAO basis set; for this, the fundamental equations are (21), (22), (36), and (39).

Appendix A

In this appendix, we present the expansion in Taylor series, about $\gamma = 1$, of the operator $\hat{V}'_{Ne}$ of the expression (33),

$$\hat{V}'_{ne}(\gamma) = -\sum_{iA} \frac{Z_A}{|\gamma\vec{r}_i - \vec{R}_A|}.$$

The expansion gives us

$$\hat{V}'_{Ne}(\gamma) = \hat{V}'_{Ne}(\gamma = 1) + (\gamma - 1)\frac{\partial}{\partial\gamma}\hat{V}'_{Ne}(\gamma)\big|_{\gamma=1} + \ldots . \quad (40)$$

But, because

$$|\vec{r}_i|^2 - \vec{r}_i \cdot \vec{R}_A = |\vec{r}_i - \vec{R}_A|^2 + \vec{r}_i \cdot \vec{R}_A - |\vec{R}_A|^2,$$

Eq. (40) becomes, until first order,

$$\hat{V}'_{Ne}(\gamma) = \hat{V}_{Ne} + (\gamma - 1)\sum_{iA} \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \ldots , \quad (41)$$

where the other terms are smaller and therefore can be neglected. Then, (41) is rewritten as

$$\hat{V}'_{Ne}(\gamma) = (2 - \gamma)\hat{V}_{Ne}.$$

Appendix B

In this appendix, we will indicate the mathematical steps to obtain Eq. (20). We begin from

$$(\hat{1}E_\ell^{(0)} - \hat{P}\hat{H}_0\hat{P})(\hat{1}E_\ell^{(0)} - \hat{P}\hat{H}_0\hat{P})^{-1} = \hat{1}. \quad (42)$$

Then, multiplying (42) by $\hat{P}$ (note that $\hat{P}^2 = \hat{P}$) we have

$$\hat{P}(\hat{1}E_\ell^{(0)} - \hat{P}\hat{H}_0\hat{P})(\hat{1}E_\ell^{(0)} - \hat{P}\hat{H}_0\hat{P})^{-1}\hat{P} = \hat{P} \quad (43)$$

and using (8) it follows that

$$E_\ell^{(0)} - \hat{P}\hat{H}_0\hat{R} = \hat{P}. \quad (44)$$

Now, with Eqs. (4)–(6) we obtain

$$(\hat{1}E_\ell^{(0)} - \hat{H}_0)\hat{R} + \frac{|\Psi_\ell\rangle\langle\Psi_\ell|}{C}\hat{H}_0\hat{R} = \hat{1} - \frac{|\Psi_\ell\langle\Psi_\ell|}{C}. \quad (45)$$

And, if we multiply (45) on the left by $\langle s|$ and on the right by $|j\rangle$ we have

$$\langle s|(\hat{1}E_\ell^{(0)} - \hat{H}_0)\hat{R}|j\rangle + \langle s|\Psi_\ell\rangle\left\langle \Psi_\ell\left|\frac{\hat{H}_0\hat{R}}{C}\right|j\right\rangle = \langle s|j\rangle - \langle s|\Psi_\ell\rangle\frac{\langle\Psi_\ell|j\rangle}{C}. \quad (46)$$

Substituting Eq. (19) into Eq. (46) and utilizing Eq. (17), we obtain

$$\langle s|(\hat{1}E_\ell^{(0)} - \hat{H}_0)\hat{R}|j\rangle + \langle s|\hat{W}|\ell\rangle\langle\ell|j\rangle = \langle s|j\rangle \quad (47)$$

and, as

$$\hat{H}_0|s\rangle = E_s^{(0)}|s\rangle, \quad (48)$$

it follows, finally, that

$$(E_\ell^{(0)} - E_s^{(0)})R_{sj} = \delta_{sj} - W_{s\ell}\delta_{\ell j}. \quad (49)$$

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References

1. Löwdin, P.-O. Adv Chem Phys 1959, 2, 207.
2. Löwdin, P.-O. J Math Phys 1962, 3, 969.
3. Löwdin, P.-O. Phys Rev A 1965, 139, 357.
4. McWeeny, R. *Methods of Molecular Quantum Mechanics;* Academic Press: New York, 1978; p. 40.
5. Löwdin, P.-O. Int J Quantum Chem 1995, 55, 77.
6. Lograd o, P. G.; Vianna, J. D. M. J Math Chem 1997, 22, 107.
7. Logrado, P. G.; Vianna, J. D. M. J Math Chem 1999, 26, 1.
8. Brown, K. M. Siam J Numer Anal 1969, 6, 560.
9. Møller, C.; Plesset, M. S. Phys Rev 1934, 46, 618.
10. Slater, J. C. Phys Rev 1929, 34, 1293.
11. Condon, E. U. Phys Rev 1930, 36, 1121.
12. Blaudeau, J. P.; McGrath, M. P.; Curtiss, L. A.; Randon, L. J Chem Phys 1997, 107, 5016.
13. Binning, R. C. Jr.; Curtiss, L. A. J Comput Chem 1990, 11, 1206.
14. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. J Comput Chem 1994, 14, 1347.
15. Ransil, B. J. Rev Mod Phys 1960, 32, 239.
16. Moscardó, F.; Pérez-Jiménez, A. J.; Cjuno, J. A. Int J Quantum Chem 1998, 19, 1899.
17. Bender, C. F.; Davidson, E. R. Phys Rev 1969, 183, 23.