
THE APPLICATION OF INNER PROJECTION TECHNIQUE
TO MANY ELECTRON SYSTEMS AS COMPARED WITH THE
COUPLED CLUSTER EXPANSION. A STUDY OF THE
PARISER-PARR-POPLE MODEL OF THE BENZENE MOLECULE

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Dedicated to Dr R. Zahradnik on the occasion of his 60th birthday.

The technique of inner projection is used for the first time in a chemical context, namely for the study of the ground state energy of the Pariser-Parr-Pople model of the benzene molecule. The lower bound for the energy is calculated for three types of parametrization. These results are compared with the "exact" energies which are obtained from full configuration interaction. It is shown that the inner projection technique provides very good lower bounds for the energy. In addition, we compare these inner projection results with those obtained by other approximative techniques, namely with the results of the Coupled Pair Many Electron Theory. A discussion of the application of the method of intermediate hamiltonians and the inner projection technique is also included.

In quantum theory, the energies of stationary states of a physical system are determined from the Schrödinger equation. However, in most cases, solving exactly the latter appears to be an impracticable task: it is then preferable to approximate the energy rather than trying to obtain its exact value. One way to subserve this purpose consists of bracketing the energy: it is thus very useful to develop techniques for the calculation of lower and upper energy bounds.

The determination of upper bounds constitutes a relatively simple problem: to this end, a variational principle is usually applied. On the other hand, the determination of lower bounds is a considerably more complicated matter. This problem has attracted the attention of many researchers; for instance, it was the subject of a series of papers by Löwdin and coworkers¹⁻¹¹. The ideas of inner projection and bracketing techniques are central to these studies. They were partly inspired by the work of

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Alexander Weinstein¹² and his school and, in particular, by the papers of Bazley and Fox¹³, built on the concept of intermediate hamiltonians.

The method of inner projection was used and refined in a series of papers^{14,18}. The concept of renormalized inner projection was introduced and applied with remarkable success¹⁵⁻¹⁸. In the next section of this paper, we will briefly present the basic ideas of the optimal inner projection technique (without renormalization) and of the method of intermediate hamiltonians. Although these methods produce in principle identical results, the optimal inner projection scheme offers some practical advantages which will be pointed out.

The estimation of lower bounds is, as previously indicated, a really intricate problem and all applications of techniques developed to meet that end, have been limited until now to one particle and two-particle systems. In this paper, the method of optimal inner projection will be applied to obtain lower bounds to the eigenvalues of Pariser-Parr-Pople hamiltonians. In particular, we shall study the lower bounds of the ground state energy of the PPP model of the benzene molecule. In doing so, this study represents a first attempt to use the concept of lower bounds in a truly chemical context.

Our future goal, for subsequent papers, is to extend the calculations of lower energy bounds to excited states as well as to study the relation between the inner projection technique and the coupled cluster theory. It is our intent to propose the concept of an approximative lower energy bound and thus allow the consideration of more realistic hamiltonians than PPP hamiltonians.

THEORETICAL

Method of Inner Projection

In this communication, the main ideas behind the method of inner projection are very briefly summarized. A complete description of the method can be found in literature¹. A shorter presentation is given in paper by Čížek and Vrscay¹⁴.

Consider the hamiltonian

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{V}, \quad (1)$$

where \mathbf{H}_0 is an unperturbed hamiltonian and \mathbf{V} the perturbation. Let $\mathbf{g} \equiv (\phi_0^{(0)}, \phi_1^{(0)}, \dots, \phi_{k-1}^{(0)})$ be a k -dimensional manifold spanned by the first k eigenfunctions $\{\phi_i^{(0)}\}$ of \mathbf{H}_0 . We then define a $k \times k$ matrix \mathbf{A} whose entries a_{ij} are given by the following expression

$$a_{ij} = v_{ij} - \sum_{l \neq 1} \frac{v_{il}v_{lj}}{\epsilon - E_{l-1}^{(0)}}, \quad (2)$$

where

$$v_{ij} = \langle \phi_{i-1}^{(0)} | \mathbf{V} | \phi_{j-1}^{(0)} \rangle, \quad (3)$$

and $E_{i-1}^{(0)}$ is the eigenvalue of \mathbf{H}_0 corresponding to the eigenfunction $\phi_{i-1}^{(0)}$.

One of the most important features of the method of inner projection is the fact that the summation in Eq. (2) is in principle not restricted to $l \leq k$. However, in well-behaved cases, this summation runs over a finite index since the perturbed elements v_{ij} vanish after some i and some j . In the case of the ground state energy of the benzene molecule, the manifold considered consists only of the ground state and biexcited state: it is then sufficient to limit the summation over the ground, biexcited, triexcited and tetraexcited states.

The final expression for the lower bound is given by

$$\varepsilon_1' = E_0^{(0)} + \sum_{i,j} v_{1i} (a^{-1})_{ij} v_{j1}, \quad (4)$$

where $(a^{-1})_{ij}$ denote an element of the inverse matrix of \mathbf{A} .

In this paper, we shall use the so-called optimal inner projection¹⁴, which is a method that produces a sequence of lower bounds iteratively. By iteration we understand that the left hand side of Eq. (4) is taken as input in Eq. (2) and that this process is repeated until the convergence is achieved. In such a way, an optimal lower energy bound is obtained for the given manifold.

Method of Intermediate Hamiltonians

Now let us partition the perturbation \mathbf{V} of the hamiltonian $\mathbf{H} = \mathbf{H}_0 + \mathbf{V}$ in the following way:

$$\mathbf{V} = \begin{bmatrix} \mathbf{M} & \mathbf{N} & \mathbf{O} \\ \mathbf{N}^T & \mathbf{P} & \mathbf{Q} \\ \mathbf{O} & \mathbf{Q}^T & \mathbf{R} \end{bmatrix}, \quad (5)$$

where \mathbf{M} is a $k \times k$ matrix whose entries M_{ij} are the elements $\langle \phi_i^{(0)} | \mathbf{H}_0 | \phi_j^{(0)} \rangle$ and $\phi_i^{(0)}$, $\phi_j^{(0)}$ are eigenfunctions of \mathbf{H}_0 belonging to the manifold \mathbf{g} , \mathbf{N} is a $k \times m$ matrix whose entries $N_{i\mu}$ are the states not in \mathbf{g} but interacting with at least one eigenfunction in the manifold \mathbf{g} . The matrices \mathbf{P} , \mathbf{Q} and \mathbf{R} represent the rest of the perturbation and are not directly used in the calculation of lower bounds in both methods. The transpose matrix of \mathbf{N} and \mathbf{Q} are denoted by \mathbf{N}^T and \mathbf{Q}^T respectively. Finally, \mathbf{O} represents the null matrix.

Let \mathbf{B} denote the $k \times (k + m)$ matrix whose entries B_{ij} are given by

$$B_{ij} = \begin{cases} M_{ij} & \text{if } i, j \leq k, \\ N_{ij} & \text{if } i \leq k \text{ and } k + 1 \leq j \leq m. \end{cases} \quad (6)$$

We then obtain a new perturbation matrix \mathbf{V}'

$$\mathbf{V}' = \mathbf{B}^T \mathbf{M}^{-1} \mathbf{B}, \quad (7)$$

where \mathbf{B}^T denotes the transpose matrix of \mathbf{B} and \mathbf{M}^{-1} the inverse matrix of \mathbf{M} . It can be shown that \mathbf{V}' has the form

$$\mathbf{V}' = \begin{bmatrix} \mathbf{M} & \mathbf{N} \\ \mathbf{N}^T & \mathbf{S} \end{bmatrix}, \quad (8)$$

where $\mathbf{S} = \mathbf{N}^T \mathbf{M}^{-1} \mathbf{N}$. We then diagonalize the intermediate hamiltonian $\mathbf{H}' = \mathbf{H}_0 + \mathbf{V}'$. The lowest eigenvalue thus obtained should be identical to the optimal lower bound obtained by the optimal inner projection technique for a given manifold \mathbf{g} .

When comparing the method of intermediate hamiltonians with the inner projection iterative scheme, the advantage in using the latter becomes clear. In this case, we are looking at a nonlinear k -dimensional problem which can easily be solved by a bracketing technique. In the method of intermediate hamiltonians, although the problem is linear, the dimension is $(k + m)$. In the case of the PPP hamiltonian of the benzene molecule, the difference between k and m is not great and thus the results obtained using both methods required similar efforts. However, for systems of ten electrons (for instance), when the value of m is much greater than k , the diagonalization of the $(k + m) \times (k + m)$ matrix needed in the method of intermediate hamiltonians, demands more work than the calculations required by the optimal inner projection technique. In addition, let us note that the method of intermediate hamiltonians requires a diagonalization which consists, in principle, in an infinitely many step procedure. Applying the optimal inner projection, the situation is similar. However, if satisfied after some iterations, we get a closed expression for the lower energy bound, provided of course that the expression for the initial upper bound was also in a closed form. This constitutes another advantage for using the inner projection technique.

Pariser–Parr–Pople Model

The use of models in theoretical chemistry and theoretical physics is very helpful as the solution of the actual problem is usually extremely tedious to get and brute force should be applied. Moreover a qualitative analysis of the results obtained by these brute force techniques is very difficult. On the other hand, models should be employed with care. Unfortunately, the majority of the existing models belongs to two categories. The first includes models which are simple and transparent but far from a true representation of reality, whereas the second includes models which are close to reality but sacrifice simplicity and transparency.

The PPP model for the description of π electrons in planar conjugated hydrocarbons¹⁹⁻³⁹ represents an exception: the mathematical structure of the PPP model is reasonably simple and transparent while, at the same time, the model delineates fairly accurately the most important features of the exact hamiltonian. Indeed, the long range behavior of electrostatic forces is well described by this model. In addition, some basis assumptions such as the ZDO (zero differential overlap) are well justified²⁵.

Let us consider alternant planar conjugated hydrocarbons in general with particular reference to the benzene molecule. Let us use second quantization for the description of the corresponding π electron system and introduce on the site (carbon atom) i , creation and destruction operators: creation operators in this site are denoted by $\mathbf{X}_{i\alpha}^+$ and $\mathbf{X}_{i\beta}^+$, where α stands for positive spin and β for negative spin, and similarly destruction operators by $\mathbf{X}_{i\alpha}$ and $\mathbf{X}_{i\beta}$. Finally, the occupation number is given by

$$n_i = \mathbf{X}_{i\alpha}^+ \mathbf{X}_{i\alpha} + \mathbf{X}_{i\beta}^+ \mathbf{X}_{i\beta}. \quad (9)$$

The PPP hamiltonian is then written in the form $\mathbf{H}_{\text{PPP}} = \mathbf{H}_0 + \mathbf{V}$ (see ref.²⁸), where

$$\mathbf{H}_0 = \sum'_{i,j} \beta_{ij} (\mathbf{X}_{i\alpha}^+ \mathbf{X}_{j\alpha} + \mathbf{X}_{i\beta}^+ \mathbf{X}_{j\beta}) \quad (10)$$

and

$$\mathbf{V} = \frac{1}{2} \sum'_{i,j} (n_i - 1) (n_j - 1) \gamma_{ij}. \quad (11)$$

The prime in Eq. (10) indicates that the summation runs only over neighbors, the β_{ij} 's are the resonance (hopping) integrals and the γ_{ij} 's the integrals of electrostatic repulsion calculated semiempirically. In this paper, three different parametrizations will be used: Pariser-Parr-Pople (PPP), Mataga-Nishimoto (MN), and Theoretical (T); see Table I. Moreover, only the physical values of the resonance integral will be considered.

TABLE I

Values of the parameters for PPP model of benzene. The different parametrization are Mataga-Nishimoto (MN), Theoretical (T), Pariser-Parr-Pople (PPP). All values are in eV

Parameter	MN	T	PPP
β	-2.3880	-2.7340	-2.3900
γ_{11}	10.8400	17.6180	10.5300
γ_{12}	5.2981	8.9239	7.300
γ_{13}	3.8551	5.5739	5.4600
γ_{14}	3.5050	4.8760	4.9000

We strongly emphasize that the operator \mathbf{V} is positive definite for the physically reasonable $\gamma_{ij}(\gamma_{ij} \geq 0)$ and this property being satisfied, the method of inner projection can be applied to the PPP hamiltonians. The π electron system of the benzene molecule is of particular interest. Benzene has a high space symmetry and therefore the resulting CI matrix for the ground state is relatively small and easy to diagonalize^{32,33}. Indeed, a matrix corresponding to the ground state is constructed from 22 states: one ground state, eight biexcited states, four triexcited states, eight tetraexcited states and one hexaexcited state. It would be possible to decrease the size of the matrix to 18×18 with the use of alternant symmetry, but we refrain from that treatment. We will thus consider a nine functions manifold, i.e. $k = 9$, and twelve functions interacting with the states in the manifold, i.e. $m = 12$. The results of applying the inner projection technique described in Theoretical are presented in the next section.

RESULTS

Coupled cluster technique (CC)⁴⁰⁻⁵⁵ or its specialized version, the Coupled Pair Many Electron Theory (CPMET)⁴⁰ has become these days a standard method for the evaluation of the ground state energy of the closed system. There is a certain similarity between CPMET and the inner projection technique. If triexcited states are omitted, both theories need the knowledge of the matrix elements between the ground state and the biexcited states, the matrix elements among biexcited states and finally, the matrix elements between biexcited states and tetraexcited states. In both

TABLE II

Correlation energy in different approximations for the sets of parameters (see Table I). The absolute values of the correlation energy are shown for the following techniques: Hartree-Fock (HF), Full Configuration Interaction (FCI), Inner Projection (IP), Coupled Pair Many Electrons Theory (CPMET) = (CCD), Configuration Interaction limited to biexcited states (B), and the linear version of the Coupled Pair Many Electrons Theory (LCPMET). The error (in parenthesis) is given in % with respect to the FCI correlation energy.

Method	MN	T	PPP
HF	0.0 (100)	0.0 (100)	0.0 (100)
FCI	1.421 (0.0)	3.261 (0.0)	0.597 (0.0)
IP	1.441 (1.4)	3.381 (3.7)	0.603 (1.0)
CPMET	1.417 (-0.3)	3.285 (0.7)	0.589 (-1.3)
B	1.314 (-7.5)	2.840 (-12.9)	0.574 (-3.9)
LCPMET	1.492 (5.0)	3.683 (12.9)	0.603 (1.0)

theories, a knowledge of the matrix elements among tetraexcited states is not required.

On the other hand, the goals of the two techniques are completely different. In CPMET, the main concern is to minimize the absolute error without attempting to determine whether the obtained energy is above or below the exact energy value. In inner projection, the objective is to obtain lower bounds: it is therefore natural to accept a worse error in absolute value as a price for the assurance of knowing that the resulting energy will be indeed a lower bound. This observation will be further discussed from a theoretical point of view in a forthcoming paper¹⁸: the present paper will be limited to the discussion of numerical results for physical values of parameters.

The results are presented in Table II. The Hartree-Fock energy is chosen as a reference and the correlation energies are presented with their corresponding error with respect to the "exact correlation energy" FCI. As expected, the best results with respect to the absolute error are obtained by the CPMET. However, the MN and PPP parametrizations produce upper bound energies when compared with the exact energy while the T parametrization produce lower bound energies. Using the inner projection iterative scheme, lower bound energies are always obtained, but the absolute error is greater than using the CPMET. Results of configuration interaction limited to biexcited states (B) are also included for completeness of our study. These results are of course upper bound for the exact energy, but the absolute error compared with the CPMET is considerably bigger. Finally, we quote for comparison the results of linear version of the CPMET. Let us note that lower (upper) bounds to the energy correspond to the upper (lower) bounds to the absolute value of the correlation energy.

In conclusion let us emphasize that this paper is only a first pilot study intended to investigate the application of the optimal inner projection method to a PPP hamiltonian. The results are very encouraging for a future two-folded extension of this work: the error of all methods as a function of β (which is playing role of coupling constant) will be first studied and secondly, the inner projection technique will be employed for systems larger than the benzene molecule. The final goal is a formulation of a method which would be applicable to more general types of hamiltonians than the PPP hamiltonians. In this case, we shall be obliged to introduce only "approximative lower bounds", but even these approximative quantities should be practically very useful.

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