

# A first-principles method to model perturbed electronic wavefunctions: the effect of an external homogeneous electric field

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## Abstract

In this Letter, we show that with the use of matrix notation to express the time-independent Schrodinger equation, it is possible to model perturbed electronic wavefunctions. Such a method makes use of first principles of the quantum mechanical theory and hence is rigorous within the only approximation due to the truncation of the perturbed Hamiltonian matrix used. Results show that for three different molecules in vacuo under an electric field, the proposed method provides reliable perturbed electronic wavefunctions at a low computational costs. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Recent advances in theoretical and computational methods have increased our knowledge of the microscopic aspects of matter. Nowadays, a huge number of electronic properties can be accessed at relatively low computational costs for differently sized systems ranging from isolated atoms to moderately large molecular clusters in vacuo [1–4]. Often it is important to evaluate some of the above properties in the presence of an external field [5–8]. In these cases, the most commonly adopted strategies are based either on standard perturbation theory or on the standard solution of the Hartree–Fock self-consistent field (HF-SCF)

problem with a perturbed electronic Hamiltonian [9–11]. For example, the effect of a static homogeneous electric field can be taken into account by simply adding to the unperturbed non-relativistic Hamiltonian operator  $\hat{H}^0$  the perturbation term  $-\mathbf{E} \cdot \hat{\boldsymbol{\mu}}$ , where  $\mathbf{E}$  is the electric field and  $\hat{\boldsymbol{\mu}}$  is the electric moment operator. Hence a standard Hartree–Fock and post-Hartree–Fock procedure, e.g., perturbation theory or multiconfigurational SCF, can be carried out. Anyway, the effect of a perturbation on the electronic properties of atoms and molecules is a long-standing problem [12], whose first-principles based solution can be directly obtained from basic quantum mechanics theory. In fact, with the use of matrix notation [13], such a problem can be reduced to the diagonalization of the perturbed Hamiltonian matrix,  $\tilde{H}$ , expressed in the unperturbed basis set, i.e., the

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eigenfunctions of the unperturbed Hamiltonian operator  $\hat{H}^0$ , which clearly diagonalizes the corresponding matrix  $\tilde{H}^0$ . Historically, such a method was only rarely adopted at molecular level and only for treating internal perturbations such as, for example, the calculation of spin–orbit coupling [14] which, within the non-relativistic theory, has to be considered as an internal perturbation. However, at the best of our knowledge, for dealing with more general perturbations, the above approach was never proposed although it shows some advantages. In fact, it is in principle, a rigorous procedure within the only practical approximation arising from truncating the dimension of the perturbed Hamiltonian matrix, that is to say the size of the unperturbed basis set is used. However, it should be remarked that the present approach could suffer from not rigorous derivation of the unperturbed eigenstates due to the well-known limitations which could arise when highly excited states are concerned. On the other hand, it appears as an investigating tool very promising for large and computationally demanding molecular systems, since the unperturbed eigenfunctions have to be evaluated only once at a given geometry, although the external perturbation is varied. Finally, it should be noted that the perturbed Hamiltonian matrix can be constructed and diagonalized nowadays, at a relatively low computational cost. In this Letter, we will report the development and implementation of such a procedure when the perturbing external field is a homogeneous static electric field. Some tests performed on sample molecules will also be shown with the aim of evaluating the actual reliability of the overall approach.

## 2. Theory

The time independent Schrodinger's equation, in matrix notation, for a perturbed system is

$$\tilde{H}c_i = \mathcal{W}_i c_i, \quad (1)$$

where  $\tilde{H} = \tilde{H}^0 + \tilde{V}$ ,  $c_i$  is the  $i$ th eigenvector of the perturbed Hamiltonian matrix  $\tilde{H}$ ,  $\mathcal{W}_i$  is the corresponding Hamiltonian eigenvalue,  $\tilde{H}^0$  is the unperturbed Hamiltonian matrix and  $\tilde{V}$  is the

perturbation energy matrix. Note that the Hamiltonian matrix and its eigenvectors can be expressed in the basis set defined by the unperturbed Hamiltonian matrix eigenvectors, and hence the element of the Hamiltonian matrix is

$$H_{l,r} = \langle \Phi_l^0 | \hat{H} | \Phi_r^0 \rangle = \mathcal{W}_l^0 \delta_{l,r} + \langle \Phi_l^0 | \hat{V} | \Phi_r^0 \rangle, \quad (2)$$

where  $\Phi_l^0$  is the  $l$ th eigenfunction of the unperturbed Hamiltonian operator,  $\mathcal{W}_l^0$  the corresponding energy eigenvalue,  $\delta_{l,r}$  the Kronecker delta and  $\hat{V}$  the perturbation energy operator. From the above equations it is evident that for obtaining the eigenvectors and eigenvalues, and hence every property, of the perturbed Hamiltonian eigenstates, we only have to diagonalize the matrix  $\tilde{H}$ , as given by Eq. (2). In this Letter we always considered molecules as described by the Born–Oppenheimer approximation, using as perturbation energy the effect of a homogeneous static electric field. Note that with these simplifications Eq. (2) becomes

$$H_{l,r} = \langle \Phi_l^0 | \hat{H} | \Phi_r^0 \rangle = \mathcal{W}_l^0 \delta_{l,r} - \mathbf{E} \cdot \langle \Phi_l^0 | \hat{\boldsymbol{\mu}} | \Phi_r^0 \rangle, \quad (3)$$

where  $\mathbf{E}$  is the electric field,  $\hat{\boldsymbol{\mu}}$  is the electric moment operator and clearly the unperturbed eigenfunctions are obtained at fixed nuclei (electronic eigenfunctions). The previous equations are exact and completely general, but involve in principle infinite dimensional matrices and vectors and hence in their exact form are practically undoable. However, if we are interested in the perturbed ground state and the first excited states, we can approximate Eq. (1) using a finite dimensional Hamiltonian matrix constructed, via Eq. (2), by a limited subspace of the unperturbed eigenstates, ranging from the ground state to a given excited one. In order to test the convergence of such an approximation we compared the results obtained for subspaces of increasing dimension. To evaluate the accuracy of the method proposed we also compared our results with those obtained by standard second-order perturbation theory, based on the same unperturbed eigenstates subset, and comparing with SCF results. Note that for a given unperturbed subset the perturbation theory results can be considered as an approximation of the solution obtained by diagonalization of the perturbed Hamiltonian matrix [12].

### 3. Computational method

In order to obtain the eigenfunctions of the unperturbed Hamiltonian, Hartree–Fock calculations were initially carried out in correspondence of the global minimum located in the full space of the coordinates within the Born–Oppenheimer hypersurface. Multi-configurational self-consistent field calculations (MCSCF) [15] of the Full Optimised Reaction Space type were then performed using active spaces of different dimensions according to the molecule under investigation. For the calculation of the off-diagonal terms of Eq. (3), basically the transition dipole vectors, the state-averaged procedure, as implemented in GAMESS US package [16] has been adopted. Since such calculations are known to be potentially affected by the quality and the dimension of the atomic basis set (ABS), differently sized ABS were then used and their effect on both the unperturbed and perturbed results qualitatively investigated. In particular, minimal STO-6G [17], ‘split valence’ 3-21G [18] and 6-311G(d,p) [19] and Dunning’s correlation consistent triple zeta [20] with p, d and diffuse sp functions added (cc-TVZ+pd) were used at this purpose. However, it should be pointed out that dimension of the ABS is computationally limiting and hence extended ABS, as cc-TVZ+pd, can only be used for molecules involving a limited number of electrons. Therefore we used a larger ABS, such as cc-TVZ+pd, only in one case. In this Letter, we investigated the reliability of the method proposed using three molecules of increasing complexity: carbon monoxide (CO), water and acrylonitrile (ACR). These three molecules were chosen as prototypical examples of small to medium sized molecular systems whose unperturbed eigenfunctions can be efficiently described using standard single-reference multiconfigurational methods with relatively small ABS. Moreover ACR provides a further advantage as the effect of a homogeneous static electric field on its electronic properties has been studied by means of a standard SCF method [10]. For carbon monoxide and water a full valence active space was used, while for acrylonitrile a subset of  $8\pi$  orbitals was selected to ensure the convergence of the unperturbed eigenstates. Once the unperturbed eigenstates were ob-

tained, they were used to build up the perturbed Hamiltonian matrix, according to Eq. (3), using for all the three molecules the first 10 roots of the MCSCF calculations. The perturbed Hamiltonian matrix was finally diagonalized using the QL algorithm [21]. The reliability of the perturbed matrix method (PMM) proposed in this Letter was tested in four ways.

- The external agreement with literature data (only in the case of the acrylonitrile molecule).
- The comparison with standard HF-SCF calculations in the presence of an external homogeneous electric field [22] as implemented in the GAMESS US package.
- The comparison with standard second-order perturbation theory (SOPT) results.
- Internal sensitivity analysis [23], i.e., the convergence of the perturbed eigenvalues, as a function of the matrix dimension used for the diagonalization.

### 4. Results and conclusions

A homogeneous field of 0.04 a.u. was applied along the unperturbed electric molecular moment and its effect on the ground and first excited states was evaluated. The MCSCF calculations were carried out using STO-6G and 6-311G(d,p) for CO, STO-6G, 6-311G(d,p) and cc-TVZ+pd for water and finally STO-6G and 3-21G for ACR. In Table 1 we report the difference between perturbed and unperturbed ground state energies as obtained from PMM method using 10 roots ( $\Delta\mathcal{W}_0^{\text{PMM}}$ ) and standard HF-SCF theory ( $\Delta\mathcal{W}_0^{\text{HF}}$ ). For all the molecules the PMM and HF-SCF results are in good agreement, with the only exception of 6-311G(d,p) CO, although even in this case they are within the same order of magnitude. Note that the HF-SCF result described in the literature [10] is consistent with our HF-SCF result and reasonably close to the corresponding PMM one. In Table 1 are also reported the shifts of the energy gap between the first excited and ground states due to the perturbation as obtained by PMM method using 10 roots ( $\Delta\Delta\mathcal{W}_{01}^{\text{PMM}}$ ). Also these results indicate that different ABSs do not provide significant changes except in the case of

Table 1

Comparison of the differences between perturbed and unperturbed ground state energies calculated with PMM method with 10 roots ( $\Delta\mathcal{W}_0^{\text{PMM}}$ ) and standard HF-SCF calculations ( $\Delta\mathcal{W}_0^{\text{HF}}$ ), using different ABS. In the last column it is also shown the shift of the first excitation energy due to the perturbation, as obtained by the PMM method with 10 roots ( $\Delta\Delta\mathcal{W}_{01}^{\text{PMM}}$ )

Molecule	ABS	$\Delta\mathcal{W}_0^{\text{PMM}}$ (a.u.)	$\Delta\mathcal{W}_0^{\text{HF}}$ (a.u.)	$\Delta\Delta\mathcal{W}_{01}^{\text{PMM}}$ (a.u.)
CO	STO-6G	-0.0022	-0.0033	$3.1 \times 10^{-3}$
CO	6-311G(d,p)	-0.0035	-0.0099	$2.5 \times 10^{-3}$
H2O	STO-6G	-0.038	-0.029	$-8.5 \times 10^{-3}$
H2O	6-311G(d,p)	-0.036	-0.038	$5.5 \times 10^{-2}$
H2O	cc-TVZ+pd	-0.0375	-0.035	$5.0 \times 10^{-2}$
ACR	STO-6G	-0.0477	-0.0775	$1.7 \times 10^{-2}$
ACR	3-21G	-0.0679	-0.1010	$1.5 \times 10^{-2}$
			(-0.1044 <sup>a</sup> )	

<sup>a</sup> Literature data from [10].

the water molecule treated at the STO-6G level. In such a case the description of the unperturbed eigenstates was not accurate providing exceedingly large excitation energies and not well-defined transition dipoles. Note that the first excitation energies were poorly affected by different ABSs, again with the exception of the water molecule at the STO-6G level. In order to

investigate the effect of the perturbed Hamiltonian matrix dimension on the accuracy and the convergence of the PMM results, we performed a sensitivity analysis, comparing PMM and SOPT predictions, separately for the three molecules studied. For CO we present data at the STO-6G level, whereas for water and ACR at the 6-311G(d,p) and 3-21G levels, respectively.

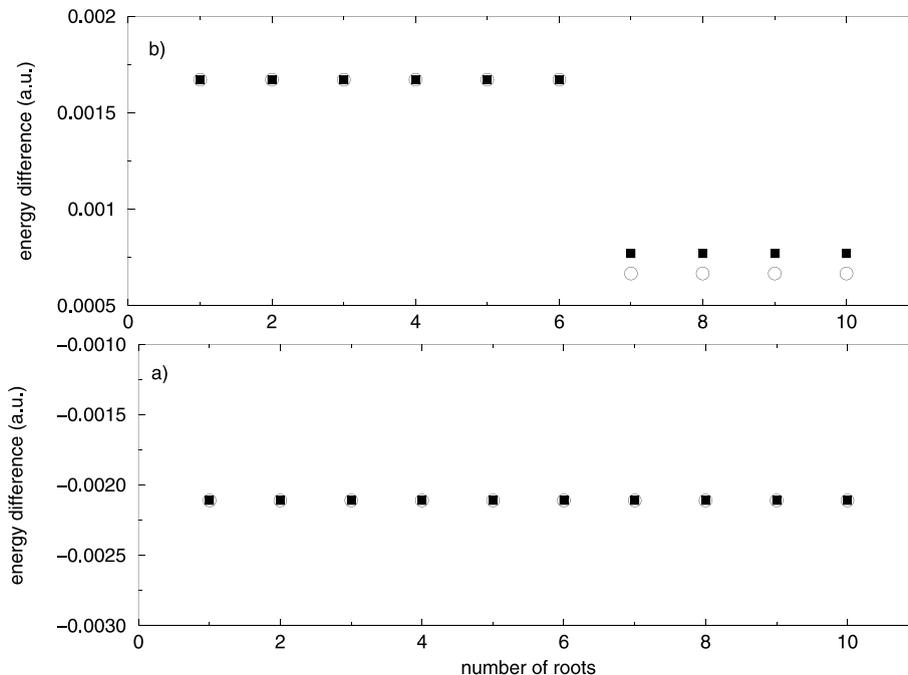


Fig. 1. (a) CO total energy differences between perturbed and unperturbed ground state as a function of the number of roots used in calculations. PMM (filled squares) and SOPT (circles). (b) CO total energy differences between perturbed and unperturbed first excited state as a function of the number of roots used in calculations. PMM (filled squares) and SOPT (circles).

#### 4.1. Carbon monoxide

In Fig. 1a we show the difference between the calculated perturbed ground state energy and the unperturbed value, for both PMM and SOPT, as a function of the the number of roots used. It is clear from the figure that these procedures provide virtually identical results and the first two roots are sufficient, for both PMM and SOPT, to reach a complete convergence for the eigenvalues. Fig. 1b shows the same comparison for the first excited state. In this case results are similar but not identical, and both PMM and SOPT converge after the seventh root. Finally we carried out the analysis of the convergence for the first two eigenvectors as obtained by PMM. Such a further analysis can provide essential information on the reliability of the use of PMM for calculating observables other than the energy. We calculated the inner product of the ground state eigenvector, obtained using an increasing number of roots, with the one obtained using the full set

of roots, i.e., 10. The same analysis was performed for the first excited state eigenvector. The results show that the perturbed ground state eigenvector is virtually identical to the unperturbed one, while the first excited eigenvector requires the first 7–8 roots to reach a very good convergence (inner product about 0.999).

#### 4.2. Water

The same analysis previously performed for CO was carried out for water and the results are reported in Fig. 2. In the case of the ground state (panel a) a good convergence was reached from the seventh root for both PMM and SOPT and the energy values are practically identical. In Fig. 2b the same analysis is shown for the first excited state: as in the ground state the values obtained from PMM and SOPT are rather similar and a full convergence is reached only with 9 roots, although the energy values change, from maximum to minimum, less then 0.01%. As for CO we per-

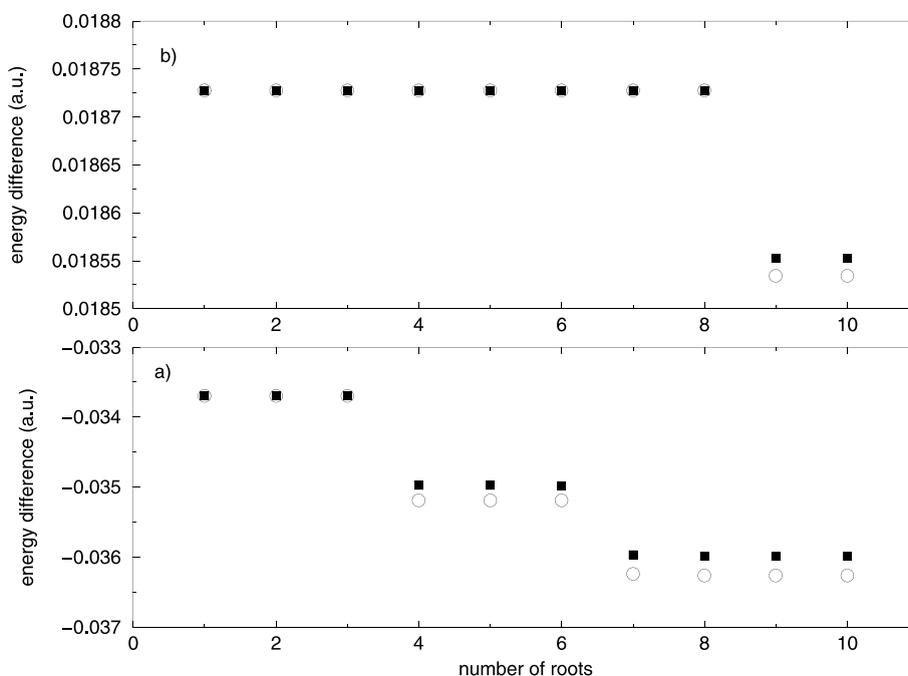


Fig. 2. (a) Water total energy differences between perturbed and unperturbed ground state as a function of the number of roots used in calculations. PMM (filled squares) and SOPT (circles). (b) Water total energy differences between perturbed and unperturbed first excited state as a function of the number of roots used in calculations. PMM (filled squares) and SOPT (circles).

formed the analysis of the ground and first excited state eigenvectors for an increasing number of roots. In this case both eigenvectors converge using the first 2–3 roots. Although not explicitly reported further calculations of the convergence of the perturbed Hamiltonian eigenvalues were carried out using cc-TVZ+pd ABS producing essentially the same result as 6-311G(d,p).

#### 4.3. Acrylonitrile

In Fig. 3a,b we show, as for CO and water, the perturbed ground and first excited state energy shift as obtained using an increasing number of roots with the 3-21G ABS. The ground state energies converge basically at the same value for both PMM and SOPT from the seventh root on, and the total relative energy change, from maximum to minimum, is about 0.15%. For the first excited state, the results from PMM and SOPT, although converged in both cases within only 4 roots, are different and their gap is as large as

0.036 a.u. The ground state eigenvector is well converged within the first 3 roots, and the first excited eigenvector reaches a good convergence at the fourth root.

#### 4.4. Conclusions

The data described in the previous subsections clearly show that the method we propose can be used to rigorously model perturbed electronic wavefunctions, at low computational costs. The method shows some intriguing practical aspects such as the possibility of obtaining information concerning perturbed ground and also excited states in the presence of an external homogeneous electric field. Note that for the three molecules the change of ABS was found to negligibly affect the convergence. We should however remark the obvious dependence of the results on the quality of the theoretical level employed for determining the set of the unperturbed wavefunctions, i.e., the possibility of obtaining reliable in- and off-diagonal

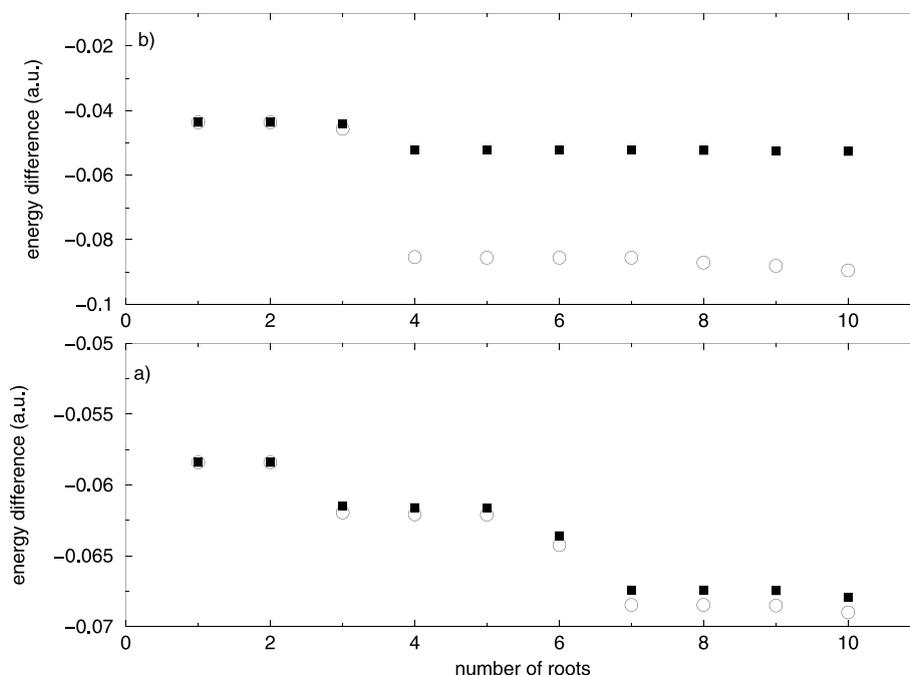


Fig. 3. (a) Acrylonitrile total energy differences between perturbed and unperturbed ground state as a function of the number of roots used in calculations. PMM (filled squares) and SOPT (circles). (b) Acrylonitrile total energy differences between perturbed and unperturbed first excited state as a function of the number of roots used in calculations. PMM (filled squares) and SOPT (circles).

matrix elements, as clearly shown by the results obtained for the water molecule described by the STO-6G ABS. It is however worth to point out that at least in the presence of the relatively simple perturbing field shown in this study, one can directly make use of experimental data, e.g., transition moment or Stark spectroscopical experiments for building up all the terms of the entire matrix. It is obviously possible that more complex type of perturbation could require higher computational costs to reach a comparable accuracy. However, because of the clear advantages of the method proposed, we expect that it can be useful in several applications, and in particular for the evaluation of ground and excited states of molecular polarizability and hyperpolarizability.

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