Theoret. Chim. Acta (Berl.) 66, 207-215 (1984)

THEORETICA CHIMICA ACTA

Use of a unitary wavefunction in the calculation of static electronic properties

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A unitary coupled cluster method is advocated in this paper for the calculation of static properties. Corresponding to the perturbed Hamiltonian $H(\lambda)$ including the relevant static property, a suitable unitary wavefunction is envisaged. It is shown that a specific nonvariational model of calculating various order static properties utilising this unitary ansatz results in simplifications compared to the previous Coupled Cluster Theories using only hole-particle excitation parameters formulated for this purpose.

Key words: Unitary ansatz—atoms and molecules—coupled cluster method—static electronic properties

1. Introduction

Recently there have been some interests in the development of theories for the calculation of static and dynamic electronic properties. Two of the major types of theories that have gained momentum in the calculation of such properties are the Coupled Cluster Methods (CCM) [1, 2] and the perturbative approach [3]. These methods have been initially formulated for the sake of electron correlation energies. Extensive applications have also been made in recent years to the calculation of correlation energies. Several reviews on the use of these theories to the subject of electron correlation energies have appeared in literature. Some reviews and significant papers have been cited in Refs. [4-11]. However, only recently attention has been turned to the adequate modification of such theories for the use in static and dynamic electronic property calculations. One of the

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NCL Communication No. 3533

earlier methods using the Coupled Cluster (CC) ansatz is to calculate the expectation value of the first order static property $\hat{0}$ of interest for a state function which is close to the exact function. Cizek [4] and Fink [12] investigated the expectation value expression in CC framework and showed it to be a sum of linked diagrams. Using a nonvariational mode of solution, a significant method was developed by Monkhorst for the calculation of static and dynamic electronic properties with the help of a CC wavefunction. The wavefunction, however, is a suitable modification of the wavefunction used for correlation energy studies. The ansatz used by Monkhorst for the static properties was described by

$$\Psi(\lambda)=e^{T(\lambda)}\phi_0 \tag{1}$$

where ϕ_0 is the single determinant reference state, $T(\lambda)$ is a suitable power series of λ, λ being the coupling parameter of the system hamiltonian with the suitable external field (defining the property of interest). Using an ansatz similar to the one of Monkhorst, the present author recently suggested a variational method for the static property calculations [2]. Similarly, the perturbation framework has been given the proper form by Sadlej and others in recent years for this purpose [3]. The system Hamiltonian was the zeroth order Hamiltonian and the coupling with the field serving as the perturbation with different order corrections giving different order static properties.

However, in the formulation of static properties by CCM, only hole-particle cluster parameters have been so far used, while in the correlation energy studies a unitary ansatz has also been tried [5, 13–17]. In this paper we present a CCM for the calculation of static electronic properties in which the ansatz $\Psi(\lambda)$ is unitary in nature. A straightforward generalisation of the nonvariational method of Monkhorst [1] using this ansatz is first made. Then it is shown that the use of a specific function (which is different from what a straightforward generalisation dictates) for projection onto the Schrodinger's equation for $H(\lambda)$ to obtain $E(\lambda)$ leads to simplified expressions for static properties. In the next section we present a brief overview of the current nonvariational [1] and variational [2] CC approaches using only hole-particle excitation parameters as well as the perturbative approach by Sadlej [3] for the calculation of static properties. Sect. 3 presents the nonvariational method with the help of the unitary ansatz. Sect. 4 contains some relevant discussions. Sect. 5 contains summary of the present work.

2. Overview of the pertinent theories

Most of the electronic properties are derivable as response of the system in the presence of external fields. For this purpose, a perturbed Hamiltonian $H(\lambda)$ is defined as,

$$H(\lambda)=H+\lambda\hat{0} \tag{2}$$

where H is the Hamiltonian of the system, $\hat{0}$ is the corresponding property operator, λ is a coupling parameter. In the approaches using the CC ansatz, the wavefunction $\Psi(\lambda)$ corresponding to $H(\lambda)$ is given in Eq. (1).

$T(\lambda)$ is expanded in a power series of λ as,

$$T(\lambda)=T+\lambda T^{(1)}+\lambda^2 T^{(2)}+\text{-----} \tag{3}$$

where the operator T is the usual logarithm of the wave operator for the wave function corresponding to field-independent Hamiltonian H. $T^{(1)}$, $T^{(2)}$ etc. operators appear as the response of the wave function in the presence of the field. In the usual nonvariational approach followed by Monkhorst

$$E(\lambda)=\langle\Phi_0|\, e^{-T(\lambda)}H(\lambda)\, e^{T(\lambda)}|\Phi_0\rangle. \tag{4}$$

A suitable power series expansion of $E(\lambda)$ is as follows

$$E(\lambda)=E+\lambda E^{(1)}+\lambda^2 E^{(2)}+\text{-----} \tag{5}$$

where, again E is the energy in the field-independent case. $E^{(1)}$, $E^{(2)}$ etc. appear due to the occurrence of the term containing the appropriate property operator $\hat{0}$ and are first, second etc. order static electronic properties. Equating various powers of λ, different orders of property can be calculated.

Specifically,

$$E^{(1)}=\langle\Phi_0|\, e^{-T}\{\hat{0}+[H, T^{(1)}]\}\, e^{T}|\Phi_0\rangle \tag{6a}$$

with the equation determining parameters of $T^{(1)}$ given by

$$\langle\Phi^*|\, e^{-T}\{\hat{0}+[H, T^{(1)}]\}\, e^{T}|\Phi_0\rangle=0 \tag{6b}$$

Φ^*'s being the relevant excited states. T-parameters are substituted from the usual Cizek's equation for calculation of correlation energy in (6b) to calculate the parameters of $T^{(1)}$. $T^{(1)}$ parameters are sufficient for the calculation of first order properties. $T^{(1)}$ can be expanded as,

$$T^{(1)}=\sum_m T_m^{(1)} \tag{7a}$$

with

$$T_1^{(1)}=\sum_{p,\alpha}\langle p|t_1^1|\alpha\rangle a_p^+ a_\alpha \tag{7b}$$

$$T_2^{(1)}=\sum_{\substack{p,q\\ \alpha,\beta}}\langle pq|t_2^1|\alpha\beta\rangle a_p^+ a_q^+ a_\beta a_\alpha \tag{7c}$$

and so on. Greek letters α, β etc. indicate hole/occupied orbitals where as p, q etc. indicate virtual orbitals. One can clearly see that in the similar equations for any order property e.g. $E^{(i)}$, parameters of $T^{(i)}$ are needed and not of higher order.

It may be noted that in Monkhorst's nonvariational approach Schrödinger's equation for the perturbed Hamiltonian $H(\lambda)$ is projected on to $\langle\Phi^*|e^{-T(\lambda)}|$ for the equations determining the relevant T-parameters and is projected onto $\langle\Phi_0|\, e^{-T(\lambda)}|$ for the values of the properties.

Recently, the present author suggested a variational method with the help of the ansatz given by the Eq. (1) [2]. A linked perturbed expectation value functional

$E(\lambda)$ is obtained

$$E(\lambda) = \langle\Phi_0|\, e^{T(\lambda)^+} H(\lambda)\, e^{T(\lambda)} |\Phi_0\rangle_{\text{Linked}}. \tag{8}$$

$E(\lambda)$ and $T(\lambda)$ have similar expansions as in Eqs. (5) and (3) respectively. A variational recipe may be followed for the calculation of the necessary different order properties. Equating powers of λ in Eq. (8), one obtains various order properties. Specifically, the first order static property $E^{(1)}$ may be written as,

$$E^{(1)} = \langle\Phi_0| N[e^{T^+}\{\hat{0} + T^{(1)^+}H + HT^{(1)}\}\, e^T] |\Phi_0\rangle_{\text{Linked}} \tag{9}$$

As for the solution of the necessary $T^{(i)}$-parameters, it was observed that if we include the necessary operators $T^{(i)}$ up to the same rank of excitation, equations obtained by differentiating $E(\lambda)$ with respect to T or $T^{(i)}$ parameters and equating powers of λ for any i will be identical. Hence, the relevant equations may, for example, be obtained by equating up to necessary powers of λ in the following system of equations equal to zero.

$$\frac{\partial E(\lambda)}{\partial T^+} = 0. \tag{10}$$

The perturbative approach followed by Sadlej starts again from the perturbed Hamiltonian as in Eq. (2) with the system Hamiltonian H providing the zeroth order Hamiltonian. A perturbative expansion of $\Psi(\lambda)$ is envisaged and k-th order property arises out of the k-th order correction term to the eigenvalue of the Schrödinger's equation for the perturbed Hamiltonian. If Hartree–Fock approximation is invoked for the zeroth order wavefunction, the values are approximate and can be corrected by the correlation perturbation series as envisaged recently by Sadlej [3].

3. Use of unitary ansatz for the calculation of static properties

The idea of unitary ansatz has been conceived by several authors e.g. VanVleck [13], Primas [14], Yaris [15], Westhaus [16], da Providencia [17] and Kutzelnigg [5]. Kutzelnigg used the ansatz in a form suitable for the correlation energy studies [5]. Instead of cluster parameters corresponding to hole-particle excitations, Kutzelnigg used as logarithm of the wave operator the anti-hermitian cluster parameters σ and cast the CCM for the correlation energies using such a unitary ansatz. It is possible in a similar vein to introduce unitary ansatz to the problem of static properties. Use of such a unitary ansatz and a suitable set of functions for projection of the corresponding Schrödinger's equation leads to simplifications for the static properties compared to the expressions derived in the Refs. 1 and 2. We write the ansatz appropriate to the perturbed Hamiltonian H(λ) as,

$$\Psi(\lambda) = e^{\sigma(\lambda)}\Phi_0 \tag{11}$$

with

$$\sigma(\lambda) = \sigma + \lambda\sigma^{(1)} + \lambda^2\sigma^{(2)} + \text{-----} \tag{12}$$

very similar to Eq. (3). However, σ, $\sigma^{(1)}$, $\sigma^{(2)}$ etc. are antihermitian such that $e^{\sigma(\lambda)}$ is unitary (λ assumed to be a real coupling parameter). Our ansatz given by Eq. (11) is a natural generalisation of the unitary ansatz used for the correlation energy to the present problem of static properties.

The Schrödinger equation for $H(\lambda)$ may be written as,

$$(H+\lambda\hat{0})\, e^{\sigma(\lambda)}\Phi_0 = E(\lambda)\, e^{\sigma(\lambda)}\Phi_0. \tag{13}$$

A straightforward generalization of the use of unitary ansatz would be to project Eq. (13) to $\langle\Phi_0|\, e^{-\sigma(\lambda)}|$ for the calculation of static properties and to $\langle\Phi^*|\, e^{-\sigma(\lambda)}|$ for obtaining the necessary cluster parameters. This would be quite similar to the Monkhorst's method except that the ansatz is unitary. In such a use of the unitary ansatz, the relevant equations would be as follows:

$$\langle\Phi_0|\, e^{-\sigma(\lambda)}H(\lambda)\, e^{\sigma(\lambda)}|\Phi_0\rangle = E(\lambda) \tag{14a}$$

$$\langle\Phi^*|\, e^{-\sigma(\lambda)}H(\lambda)\, e^{\sigma(\lambda)}|\Phi_0\rangle = 0. \tag{14b}$$

We can get expressions similar to the ones in Ref. [1] for $E^{(1)}$, $E^{(2)}$ etc. However, it may be noted that in such a case $E(\lambda)$ as obtained by Eq. (14a) would be identical to the perturbed energy functional $\langle\Psi(\lambda)|H(\lambda)|\Psi(\lambda)\rangle/\langle\Psi(\lambda)|\Psi(\lambda)\rangle$ using the ansatz (11).

However, as stated earlier, if we use a different function for projection in Eq. (14a), we get an equation for $E(\lambda)$ which gives more simplified expressions for $E^{(1)}$, $E^{(2)}$ etc. Let us project Eq. (13) on to $\langle\Phi_0|\, e^{-\sigma}|$ (not $\langle\Phi_0|\, e^{-\sigma(\lambda)}|$) to obtain,

$$\langle\Phi_0|\, e^{-\sigma}H(\lambda)\, e^{\sigma(\lambda)}|\Phi_0\rangle = E(\lambda)\langle\Phi_0|\, e^{-\sigma}\, e^{\sigma(\lambda)}|\Phi_0\rangle. \tag{15}$$

However, to derive equations for the cluster parameters σ, $\sigma^{(1)}$, $\sigma^{(2)}$ etc. the Schrödinger's equation (13) is projected again to $\langle\Phi^*|\, e^{-\sigma(\lambda)}|$ as in Eq. (14b) so that Eq. (14b) serves as an equation determining the cluster parameters. We will show later in this section the simplifications afforded by the use of Eq. (15) instead of Eq. (14a).

Using the $e^{T(\lambda)}|\Phi_0\rangle$ ansatz, Monkhorst showed that the nonvariational energy $E(\lambda)$ obtained by projecting onto $\langle\Phi_0|\, e^{-T(\lambda)}|$ is identical to the perturbed energy functional when all possible T_n-clusters are taken into account such that for the exact state $E^{(1)}$ obtained by the nonvariational method (i.e. nonvariational method to calculate $E(\lambda)$) is identical to $\langle\hat{0}\rangle$ (a restatement of Hellmann-Feynmann theorem). In the case of the unitary ansatz the nonvariational method of obtaining $E(\lambda)$ through Eq. (14a) leads to results identical to the perturbed energy functional as noted earlier. However, even in the present method of projection envisaged here using unitary ansatz it can similarly be shown that when all σ clusters are included, $E(\lambda)$ defined from Eq. (15) (by the projection on to $\langle\Phi_0|\, e^{-\sigma}|$ as advocated here) is identical to the perturbed energy functional utilising unitary ansatz i.e.

$$E'(\lambda) = \langle\Phi_0|\, e^{-\sigma(\lambda)}H(\lambda)\, e^{\sigma(\lambda)}|\Phi_0\rangle \tag{16}$$

(Norm of $\Psi(\lambda)$ is unity in this case).

This can easily be seen because of the following identities,

$$\begin{aligned}\langle\Phi_0|\, e^{-\sigma}H(\lambda)\, e^{\sigma(\lambda)}|\Phi_0\rangle &= \langle\Phi_0|\, e^{-\sigma}\, e^{\sigma(\lambda)}(e^{-\sigma(\lambda)}H(\lambda)\, e^{\sigma(\lambda)})|\Phi_0\rangle\\ &= \langle\Phi_0|\, e^{-\sigma}\, e^{\sigma(\lambda)}|\Phi_0\rangle\langle\Phi_0|\, e^{-\sigma(\lambda)}H(\lambda)\, e^{\sigma(\lambda)}|\Phi_0\rangle\\ &\quad +\sum_e \langle\Phi_0|\, e^{-\sigma}\, e^{\sigma(\lambda)}|\Phi_e^*\rangle\langle\Phi_e^*|\, e^{-\sigma(\lambda)}H(\lambda)\, e^{\sigma(\lambda)}|\Phi_0\rangle\\ &= \langle\Phi_0|\, e^{-\sigma}\, e^{\sigma(\lambda)}|\Phi_0\rangle\langle\Phi_0|\, e^{-\sigma(\lambda)}H(\lambda)\, e^{\sigma(\lambda)}|\Phi_0\rangle \qquad (17)\end{aligned}$$

(because of the resolution of identity and Eq. (14b)). But in the case of approximation function $\Psi(\lambda)$, $E(\lambda)$ defined through Eq. (15) would not be identical to $E'(\lambda)$. The relation,

$$\langle\hat{0}\rangle = \frac{\partial E'(\lambda)}{\partial\lambda}\bigg|_{\lambda=0} = \frac{\partial E(\lambda)}{\partial\lambda}\bigg|_{\lambda=0} = E^{(1)} \qquad (18)$$

($E^{(1)}$ calculated through Eq. (15) and Eq. (5)) does not strictly hold good in such approximate case. However, as pointed out by Monkhorst [1], in such cases $E^{(1)}$ is closer to the exact answer. In such cases also, we associate $E^{(i)}$ as the i-th order property. We will now derive the expressions for $E^{(1)}$, $E^{(2)}$ etc. through the use of Eq. (15) and show the simplifications obtained. We observe that $e^{\sigma}\Phi_0$ satisfies the Schrödinger's equation for the field-independent system Hamiltonian,

$$H\, e^{\sigma}\Phi_0 = E\, e^{\sigma}\Phi_0 \qquad (19a)$$

such that

$$E = \langle\Phi_0|\, e^{-\sigma}H\, e^{\sigma}|\Phi_0\rangle. \qquad (19b)$$

Eq. (19b) corresponds to λ-independent terms of Eq. (15). The equation corresponding to the terms linear in λ is given by,

$$\begin{aligned}&\langle\Phi_0|\, e^{-\sigma}H\sigma^{(1)}\, e^{\sigma}|\Phi_0\rangle + \langle\Phi_0|\, e^{-\sigma}\hat{0}\, e^{\sigma}|\Phi_0\rangle\\ &\quad = E\langle\Phi_0|\, e^{-\sigma}\sigma^{(1)}\, e^{\sigma}|\Phi_0\rangle + E^{(1)}\langle\Phi_0|\, e^{-\sigma}\, e^{\sigma}|\Phi_0\rangle. \qquad (20)\end{aligned}$$

With the use of Eq. (19a) one obtains

$$E^{(1)} = \langle\Phi_0|\, e^{-\sigma}\hat{0}\, e^{\sigma}|\Phi_0\rangle \qquad (21)$$

for the expression of the first order static property. The nonvariational method of Monkhorst [1] or the variational method of the present author [2] needs the knowledge of $T^{(1)}$ parameters for the calculation of $E^{(1)}$ as can be seen in Eqs. (6a) and (9) respectively. But here $E^{(1)}$ turns out as the expectation value of the property operator $\hat{0}$ with respect to the original system wavefunction alone. However, the ansatz unlike the ones used in Refs. 1 and 2 is unitary. Similarly, the expression for any second order property $E^{(2)}$ may also be derived. We will observe that the expression for $E^{(2)}$ does not need the knowledge of $\sigma^{(2)}$ but only up to $\sigma^{(1)}$. This advantage is obtained if the framework of unitary ansatz is used and Eq. (15) is used instead of Eq. (14a). Writing in detail the equation corresponding to quadratic terms in λ, we obtain

$$\begin{aligned}
&\langle\Phi_0|\, e^{-\sigma}H\sigma^{(2)}\, e^{\sigma}|\Phi_0\rangle+\langle\Phi_0|\, e^{-\sigma}H\sigma^{(1)^2}\, e^{\sigma}|\Phi_0\rangle+\langle\Phi_0|\, e^{-\sigma}\hat{0}\sigma^{(1)}\, e^{\sigma}|\Phi_0\rangle\\
&\quad = E\langle\Phi_0|\, e^{-\sigma}\sigma^{(2)}\, e^{\sigma}|\Phi_0\rangle+E\langle\Phi_0|\, e^{-\sigma}\sigma^{(1)^2}\, e^{\sigma}|\Phi_0\rangle\\
&\qquad + E^{(1)}\langle\Phi_0|\, e^{-\sigma}\, e^{\sigma}\sigma^{(1)}|\Phi_0\rangle+E^{(2)}\langle\Phi_0|\, e^{-\sigma}\, e^{\sigma}|\Phi_0\rangle
\end{aligned} \tag{22}$$

whence it follows that

$$E^{(2)}=\langle\Phi_0|\, e^{-\sigma}\hat{0}\sigma^{(1)}\, e^{\sigma}|\Phi_0\rangle \tag{23}$$

(with the use of $\langle\Phi_0|\sigma^{(1)}|\Phi_0\rangle=0$ and Eq. [19a]).

Thus a lower order σ would specify a higher order static property. The expression for $E^{(1)}$ has a proper multi-commutator structure. However, for higher order static properties calculated by Eq. (15) as advocated here such elegant structure (as in Monkhorst's method [1]) may not be present.

Taking cue from Kutzelnigg's work [5], $\sigma^{(i)}$ may be written as,

$$\sigma^{(i)}=T^{(i)}-T^{(i)^+} \tag{24a}$$

$$\sigma=T-T^+ \tag{24b}$$

T, $T^{(1)}$, $T^{(2)}$ etc. have usual meaning of hole-particle excitation parameters (as used in works cited in Refs. [1] and [2]).

4. Discussions

The nonvariational $E(\lambda)$ as defined through Eq. (15) may also be seen to be identical to a bivariational expression for perturbed Hamiltonian $H(\lambda)$ defined by

$$\langle\tilde{\Psi}|(H(\lambda)-E(\lambda))|\Psi(\lambda)\rangle=0 \tag{25}$$

with $\Psi(\lambda)$ as defined in Eq. (11) and $\tilde{\Psi}$ as $e^{\sigma}\Phi_0$ which is a unitary ansatz for the system Hamiltonian H alone. Bivariational expressions suitable for correlation energy studies were used by Jankowski et al. [18].

The structure of the expressions for $E^{(i)}$ are quite similar to a perturbative structure where a lower order correction to the wavefunction specifies the higher order corrections to the energy. Let us start from H as the zeroth order Hamiltonian with $\hat{0}$ as the perturbation term, λ being the perturbation parameter. However, we consider as the zeroth order wavefunction not the Hartree-Fock wavefunction but a CC wave function for the system. Again if we consider a unitary ansatz for the system Hamiltonian [5, 13-17], the zeroth order wavefunction in this model perturbative problem is given by,

$$\Psi_0=e^{\sigma}\Phi_0 \tag{26}$$

Φ_0 being the Hartree-Fock function such that $E^{(1)}$, the first order correction, is given by Eq. (21) in the perturbation framework. There is a similarity with perturbative structure for perturbation corrections are obtained by projection of the Schrödinger equation on to the zeroth order CC wavefunction and equating powers of λ. With unitary CC ansatz $e^{\sigma}\Phi_0$ as the zeroth order wavefunction, Eq. (15) is precisely an equivalent approach. Indeed, if we view ansatz (11) as a perturbation expansion in λ for the model perturbation problem outlined above and associate $\sigma^{(1)}\, e^{\sigma}\Phi_0$ as the first order correction to the wavefunction, $E^{(2)}$ obtained by the unitary CC method as in Eq. (23) is precisely the perturbative equivalent. *However, we are emphasising a structural similarity only.*

5. Summary

If we use a unitary CC ansatz for the calculation of static properties and project Schrödingers equation for the appropriate perturbed Hamiltonian $H(\lambda)$ onto $\langle\Phi_0|\, e^{-\sigma}|$ (where $e^{\sigma}\Phi_0$ is the wavefunction corresponding to the system Hamiltonian H only) we obtain expressions for static properties for which the knowledge of lower order cluster parameters is sufficient. The expression for $E(\lambda)$ in such a method is akin to a bivariational expression.

Acknowledgments. The author is grateful to Dr. Debashis Mukherjee of the Indian Association for the Cultivation of Science, Calcutta from whom he has learnt the CCM. The author also acknowledges the kind interest taken by Dr. A. P. B. Sinha of the National Chemical Laboratory, Pune during the progress of this work.

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Received June 1, 1984