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On the uncorrelated reference for calculation of properties

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Summary. We consider various possibilities for the uncorrelated reference for the calculation of properties. According to the philosophy of Löwdin, to whom this volume is dedicated, the uncorrelated reference state for response properties ought to be taken as the unperturbed Hartree–Fock state for properties of all orders in the applied field. Frequently, however, it is operationally convenient to use the coupled Hartree–Fock like results as a standard of comparison for second- and higher-order properties, even though this is not consistent with Löwdin's choice for the uncorrelated reference state. In this method the reference state is the perturbed Hartree–Fock state. Numerical examples demonstrate a rather large difference between the two uncorrelated references. We consider the pros and cons of each choice.

Key words: Correlation – Properties – Polarization propagator – Coupled Hartree–Fock – Random phase approximation

1. Introduction

Perhaps the premier persistent problem confronting formal and computational quantum chemistry over the past two score years is that of electron correlation. The first thorough analysis of the effect of correlation on a calculated property, energy, was provided by Löwdin in the series of papers [1–3] to which this volume is dedicated, and in an extension [4] to it. Here he introduced a strict and logical definition of the correlation energy. He was aided by the variation principle, which guarantees that more accurate wavefunctions lead to not higher total energies, the result of a better description of the correlation (the complicated motions electrons may undergo in their attempts to avoid one another). There is, however, no analog of the variation principle which is useful for properties other than total energy, although the flexibility of the wave function obviously retains its importance. It is for this reason that it would be desirable to develop a standard of comparison to help evaluate calculated molecular properties, much as Löwdin's standard has been useful in the evaluation of calculated energies. What that standard should be is, however, not obvious.

The correlation problem was first addressed in solid-state physics nearly sixty years ago when Wigner worried about "... statistical connections of positions of different electrons ..." [5] in the context of an independent particle model (IPM) [5–8]. He was interested in "... the statistical connection between electrons with antiparallel spin ($\sigma_1 = -\sigma_2$) and between those with parallel spin ($\sigma_1 = \sigma_2$)". Wigner referred to the energy lowering attendant on the use of wavefunctions which allowed such a connection as the "correlation energy", but did not offer an operational definition of it.

Subsequently, the correlation problem was formulated in an elegant manner by Löwdin [3] in terms of the second-order density matrix. He proposed to use the Hartree–Fock (HF) solution as the uncorrelated reference state, in which case the statistical connection among particles with parallel spin is adequately described as a consequence of the Pauli principle and the antisymmetry of the HF wavefunction (the Fermi hole). The problem is thus reduced to a treatment of correlation in pairs of electrons with antiparallel spin.

The preceding discussion deals explicitly with energy. There are, however, many properties of atoms, molecules and solids other than total energy, which, for example, arise from the response of the system to an external (or internal) perturbation and which are both interesting and amenable to calculation. It is desirable to have a fixed point of reference for property calculations to serve the same function as the HF energy does for energies. Determination of such a fixed point is more difficult for properties other than total energies, as we have neither a variational theorem nor a good estimate of the exact, non-relativistic result to guide us.

In this contribution we will, in the spirit of Löwdin, consider the calculation of molecular properties, and the effect of inclusion of correlation on such calculations. It seems that the situation now regarding the calculation of molecular properties is in much the same state as energy calculations were when Löwdin wrote on correlation and energy in 1955 and is thus ripe for discussion.

We will discuss the notion that it may be appropriate to use a definition for the uncorrelated limit for second- and higher-order properties that deviates from Löwdin's definition of the uncorrelated limit for zeroth-order properties in order to conform to the conventional way of defining zeroth-order in property calculations. Such a definition is based on the Finite Field method and differs in substance from the Löwdin definition on the point of whether the perturbing field should be included in the unperturbed Hamiltonian [9]. We will illustrate that the magnitude of the correlation contribution is very different for the two ways of defining zeroth-order for second- and higher-order properties.

2. Correlation and properties

2.1 Löwdin's definition

Löwdin wrote (exact) solutions for the stationary states Ψ_i^{ex} of the Schrödinger equation for a Hamiltonian, H:

$$H\Psi_i^{ex} = E_i\Psi_i^{ex} \tag{1}$$

in the form:

$$\Psi_i^{ex} = \Psi_i^{HF} + \Psi_i^{corr} \tag{2}$$

where the Ψ_i^{HF} are Slater determinantal solutions to the Hartree–Fock equations for the same operator H, and Ψ_i^{corr} represents the "correlation error" [4] in the wavefunctions. The associated correlation energy is then defined as:

$$E_{corr} = \langle H \rangle_{av} - E_{HF}. \tag{3}$$

As stated by Löwdin [4]:

> "The correlation energy for a certain state with respect to a specified Hamiltonian is the difference between the exact eigenvalue of the Hamiltonian and its expectation value in the Hartree–Fock approximation for the state under consideration".

As energy was, at that time, the quantity of primary interest to calculate, the Hartree–Fock approximation became, and remains, the standard of comparison in the discussions of correlation, and, *de facto*, in all of quantum chemistry.

2.2 Properties

Now let us turn to properties. Consider a system in an external field, F. The Hamiltonian may be written:

$$H = H_0 + V(F) \tag{4}$$

where H_0 describes the unperturbed system and $V(F)$ its interaction with the perturbing field. Then, following Kutzelnigg [10], one can conveniently divide up the interesting response propeties of the system [11] according to the order in which the perturbing field appears in their calculation [12]:

1. Zeroth-order properties – properties which depend on the energy only. These are the static properties (frequently independent) obtainable from the potential energy surface for the system and have to do with structure and energies.

2. First-order properties – static properties that can be obtained as expectation values of an appropriate operator between specific wavefunctions. Such quantities as dipole moment, moments of the charge distribution and other one-electron properties belong to this class.

3. Second-order properties – these static and dynamic (frequency dependent) properties correspond to second-order perturbation terms and include polarizatilities, magnetizabilities, and moments of the oscillator strength distributions.

4. Third-order properties – those properties that arise in third-order perturbation theory, and comprise, for example, the first hyperpolarizability [13], two photon transition moments [14] and transition moments between excited states [15].

Higher-order properties have also been characterized [16]. The question of correlation is of importance for all classes of properties, while the definition of Löwdin only applies explicitly to zeroth-order properties. It is our purpose to discuss the problem of correlation for higher-order properties as well.

There are three approaches which have traditionally been employed in evaluating properties. In the finite field method, the wavefunction is evaluated in the presence of the perturbing influence, and moment expansions are obtained by numeric differentiation. Rayleigh–Schrödinger perturbation theory expresses the perturbed wavefunction in terms of unperturbed functions, then analytically equates properties order-by-order from a partitioned Hamiltonian. Finally, propagator techniques extract the desired property directly from the response of the system to the perturbation. The following sections will consider the correlation problem for each class in turn.

2.3 *The finite field approach*

The finite field method [16] is based on a power series expansion of the field-dependent total energy. For example using the Hamiltonian of Eq. (4) the normalized energy functional becomes:

$$E(F) = \langle \Psi(F) | H | \Psi(F) \rangle = E_0 + \left(\frac{\partial E}{\partial F} \right)_{F=0} F + \frac{1}{2} \left(\frac{\partial^2 E}{\partial F} \right)_{F=0} F^2 + \cdots \tag{5}$$

where the nth-order moment of the field then is:

$$\frac{\partial^n}{\partial F^n} \langle \Psi(F) | H | \Psi(F) \rangle |_{F=0}. \tag{6}$$

For perturbations such as the electric dipole interaction:

$$V = -e\boldsymbol{F} \cdot \boldsymbol{r} \tag{7}$$

the Hellmann–Feynman theorem holds for variationally determined wavefunctions, so that the first-order term in the expansion series, the dipole moment, may be simply evaluated from the unperturbed wavefunction:

$$\mu_i = \frac{\partial}{\partial F} \langle \Psi_i(F) | H | \Psi_i(F) \rangle |_{F=0} = \langle \Psi_i(F=0) | -er | \Psi_i(F=0) \rangle. \tag{8}$$

In the instance that the Hellmann–Feynman theorem is fulfilled, the correlation contribution to a first-order property could thus be evaluated as:

$$A_{corr} = \langle \Psi_i^{ex} | A | \Psi_i^{ex} \rangle - \langle \Psi_i^{HF} | A | \Psi_i^{HF} \rangle. \tag{9}$$

This scheme maintains a formal connection to the Löwdin definition of correlation energy. The important difference is, however, that the zeroth-order Hamiltonian (H) differs according to property, and the wavefunction (approximate, exact or HF) is property dependent as well.

It should be noted that the $F \rightarrow 0$ limit of the Finite Field method gives the Coupled Hartree–Fock (CHF) scheme, which is equivalent to the static limit of the Random Phase Approximation (RPA) or to the Time Dependent Hartree–Fock (TDHF) scheme. The main advantage of this method is that it is operationally easy to implement (although fraught with technical difficulties). One simply calculates the property at a variety of perturbing field strengths and differentiates the result numerically, typically by taking differences of lower moments. It has been used widely for static first-, second- and higher-order properties. Recently, there has been much progress made in avoiding numerical differentiation by differentiating the energy expression analytically and calculating the resulting matrix elements directly [17, 18], thus avoiding numerical difficulties and reducing the computational effort and error. In either case, comparison of the result of a HF calculation to the exact one will indicate the importance of correlation in calculation of the property under consideration.

The finite field scheme also allows for an increase in its level of correlation, but not in as regular and systematic a way as does the propagator scheme (*vide infra*). Instead of increasing correlation via increasing the order of perturbation theory through which the problem is solved, one must first choose an ansatz for the correlated wavefunction: MCSCF, CI, MBPT or coupled cluster, for example. Increasing the level of correlation is then accomplished in a way appropriate to the ansatz wavefunction. It then becomes difficult to compare correlated calculations using different ansatz wavefunctions. In addition, the frequency dependence of second- and higher-order dynamic properties does not emerge naturally, and must be in some sense grafted on to the calculation [17].

In this definition of the uncorrelated reference, that is, if the perturbed HF solution is chosen as zeroth-order, as some authors are wont to do, RPA, is then zeroth-order.

2.4 Rayleigh–Schrödinger perturbation theory

Rayleigh–Schrödinger perturbation theory (RSPT) has pedagogical value from both the standpoint of examining the correlation problem and the analytic evaluation of static field properties. We will examine RSPT in both contexts. The formalism, which is discussed elsewhere [19], is based on expanding the Hamiltonian, wavefunction, and energy in terms of an ordering parameter, λ:

$$\begin{aligned} H &= H_0 + \lambda V \\ \Psi_i &= \psi_i^{(0)} + \lambda \psi_i^{(1)} + \lambda^2 \psi_i^{(2)} + \cdots \\ E_i &= E_i^{(0)} + \lambda E_i^{(1)} + \lambda^2 E_i^{(2)} + \cdots \end{aligned} \tag{10}$$

then collecting terms of the same order:

$$\begin{aligned} E_i^{(0)} &= \langle \psi_i^{(0)} | H_0 | \psi_i^{(0)} \rangle \\ E_i^{(1)} &= \langle \psi_i^{(0)} | V | \psi_i^{(0)} \rangle \\ E_i^{(2)} &= \langle \psi_i^{(0)} | V | \psi_i^{(1)} \rangle . \end{aligned} \tag{11}$$

The result of RSPT coalesces with the finite-field expression at first-order. The perturbed wavefunctions are expanded from complete sets of unperturbed wavefunctions, leading to familiar sum-over-states expressions, e.g. for second-order properties:

$$E_i^{(2)} = \sum_{n \neq i} \frac{\langle \psi_i^{(0)} | V | \psi_n^{(0)} \rangle \langle \psi_n^{(0)} | V | \psi_i^{(0)} \rangle}{E_i^{(0)} - E_n^{(0)}} . \tag{12}$$

The correlation problem is studied in RSPT following the Möller–Plesset (MP) scheme [20]. The Fock operator is defined to be the zeroth-order Hamiltonian, while the perturbation consists of the electron-electron interaction less the one-electron Fock potential, i.e. the fluctuation potential. When partitioned thus, the HF energy is correct through first-order in the electron interaction:

$$E_i^{HF} = E_i^{(0)} + E_i^{(1)} . \tag{13}$$

Upon convergence of an *external perturbation-free* HF self-consistent field procedure, we arrive at the first order MP (MP1) energy which is consistent with Löwdin's uncorrelated reference state for energy. As in the previous section, it may then be advantageous to choose the field-dependent HF solution as the uncorrelated reference state for properties. The two kinds of HF methods differ by the latter's induced electronic relaxations. These effects can and will be quantified in the course of our discussion.

Turning now to RSPT properties, the word "correlation" has often been rather cavalierly used. We illustrate this by examining a second-order RSPT property, into which we introduce an hierarchy of unperturbed functions. A simplistic approach to second-order RSPT for normal one-electron perturbations is uncoupled HF [21], which, for a property corresponding to operators P and Q, takes the form:

$$E^{(2)}_{PQ} = \sum_{a,p} \frac{\langle \phi_p | P | \phi_a \rangle \langle \phi_a | Q | \phi_p \rangle}{\epsilon_p - \epsilon_a} \tag{14}$$

where the sums $p, q, r, \ldots$ and $a, b, c, \ldots$ run over occupied and virtual orbitals, respectively; ϕ_p is the pth HF orbital and ϵ_p is its HF orbital energy. This will be the zeroth-order (in terms of correlation) expression. If the RSPT perturbed wavefunction is represented by a single-replacement determinant, the following result is obtained:

$$E^{(2)}_{PQ} = \sum_{a,p} \frac{\langle \phi_p | P | \phi_a \rangle \langle \phi_a | Q | \phi_p \rangle}{\epsilon_p - \epsilon_a - 2\langle pp \mid aa \rangle + \langle pa \mid pa \rangle} \tag{15}$$

where $\langle pp \mid aa \rangle = \int \phi_p^*(1)\phi_p^*(2)(1/r_{12})\phi_a(1)\phi_a(2)d(1)d(2)$. This has been referred to as the single transition approximation (STA) [22]. In Sect. 3 we refer to this level of approximation as HF for properties.

The matrix elements here have been formulated over HF single-determinantal wavefunctions, and therefore satisfy the criteria of the "uncorrelated" reference based on the language of Löwdin. However, there are several problems with this definition. Foremost, the expression in this form is not rotationally invariant, which is unacceptable on physical grounds. The reason for this is that there is no coupling between the excited states represented by one single-replacement determinant. However, a linear combination of such single-replacement functions restores this property, with the expansion coefficients variationally chosen through the monoexcited configuration interaction (MECI) procedure.

In practice, the CI matrix diagonalization and subsequent transformation steps are not necessary provided that the inverse of the MECI matrix is computed. Preferably, the expression is solved using reduced linear equation methods [23], so that large matrices may be dealt with efficiently. The second-order property then has a general matrix form:

$$E^{(2)}_{PQ} = \boldsymbol{P}^{\dagger} A^{-1} \boldsymbol{Q} \tag{16}$$

where the energy representation is now a full matrix which reflects the coupling between states:

$$A_{pa,qb} = (\epsilon_p - \epsilon_a)\delta_{pq}\delta_{ab} - 2\langle pq \mid ab \rangle + \langle pa \mid qb \rangle. \tag{17}$$

The MECI property calculation appears to exceed the limit of the Löwdin definition. In fact, this procedure is often referred to as a "correlated calculation", because of the inclusion of a CI energy representation. However, based on the analysis in the previous and following sections, this conjecture proves to be false.

2.5 The response function approach

Response functions are polarization propagators [24] which express order-by-order the density disturbance of a system subjected to an external perturbation [25]. The induced linear response hence determines properties at second-order. In the spectral representation, the linear response function is written:

$$\langle\langle P; Q\rangle\rangle_{\omega} = \sum_{n} \left\{ \frac{\langle 0|P|n\rangle\langle n|Q|0\rangle}{\omega - E_n + E_0} - \frac{\langle 0|Q|n\rangle\langle n|P|0\rangle}{\omega + E_n - E_0} \right\} \tag{18}$$

where P and Q again refer to two external/internal perturbations appropriate to the property (e.g. $P = Q = -e\boldsymbol{r}$ for dynamic dipole polarizations), and ω is the frequency of perturbing influence Q. The details of the derivation are discussed elsewhere [26]. Of course, the results of response theory are identical to those obtained from time-dependent perturbation theory [19]. In addition to the linear response, the quadratic [27, 28] and higher [28] response functions have been characterized, and are now being examined [13, 29, 30].

Equation (18) is an exact expression generated by inserting complete sets of states into the time-domain propagator, followed by its Fourier transform [26, 31]. Computationally tractable forms are obtained from the moment expansion of the propagator equation of motion [32, 33], which leads to:

$$\langle\langle P; Q\rangle\rangle\omega = (B^{\dagger} \mid T^{\dagger})(T^{\dagger} \mid \omega\hat{1} - \hat{H} \mid T^{\dagger})^{-1}(T^{\dagger} \mid A). \tag{19}$$

Equation (19) defines the superoperator binary product [33] for number-conserving operators as a commutator over the reference function:

$$(B^{\dagger} \mid T^{\dagger}) \equiv \langle 0|[B, T^{\dagger}]|0\rangle \tag{20}$$

and $T^{\dagger}$ represents the complete manifold of excitations.

Approximations to Eq. (19) result from the choice of reference function $|0\rangle$ and restrictions to the excitation space [25]. For instance, if $|\mathrm{HF}\rangle$ is used as $|0\rangle$ and $\boldsymbol{T}$ is truncated to particle-hole excitations and de-excitations, the Random Phase Approximation (RPA) to the propagator is obtained [26, 31]. Through a series of transformations to the RPA eigenvalue problem [34], Eq. (19) may be cast in the form of the spectral representation (Eq. (18)). This canonical formulation is advantageous, as dynamic properties are readily obtainable for a wide range of frequencies, with different properties quickly computed by insertion of the appropriate transition moments. However, the sum must be over the complete set of excitations for properties calculated in this way to be correct, as we have shown, for example, for the Thomas–Reiche–Kuhn sum rule and mean excitation energy (cf. Eq. (23)) of atoms [35] and molecules [36].

Instead of solving the complete eigenvalue problem, the polarization propagators are obtained using direct methods. For instance, the RPA propagator for static field properties (eigenvalue to CPHF) can be written in the form [26]:

$$\langle\langle P; Q\rangle\rangle_{\omega=0} = V_P^{\dagger}(\boldsymbol{A} - \boldsymbol{B})^{-1}V_Q. \tag{21}$$

In Eq. (21), the matrix $\boldsymbol{A}$ retains the form of Eq. (17), but we see the energy representations being augmented by elements of the $\boldsymbol{B}$ matrix:

$$\boldsymbol{B}_{pa,qb} = \langle pb \mid qa\rangle - 2\langle pa \mid qb\rangle. \tag{22}$$

To avoid matrix diagonalization, reduced linear equations methods may be used to solve $\boldsymbol{C} = (\boldsymbol{A} - \boldsymbol{B})^{-1}V_Q$. From a power series expansion of this expression, it has been shown [23] that this solution is equivalent order-by-order to iteration for the coefficients of coupled-perturbed HF (CPHF) [37].

Based on the arguments in the preceding section, it would seem, then, that RPA represents a compelling case as the uncorrelated reference of property calculations. However, one can pose arguments to the contrary. It was shown some time ago [38] that RPA is the consistent *first* order polarization propagator approximation, the perturbation being the fluctuation potential. Another major point of contention arises in consideration of vertical transition energies. These values may be calculated as poles of the propagator (but have no equivalent in the CPHF formulation). When viewed in the language of configuration interaction [39], the RPA representation of this property (of the energy) includes contribution from single configurations and limited number of doubly-excitations. Also, an inconsistency develops when the RPA/CPHF comparison is taken beyond the single-determinantal reference. For instance, the Second Order Polarization Propagator (SOPPA) is developed using a Møller–Plesset second-order reference function [25]. However, the results obtained using SOPPA differ from those computed from MP2 using field-perturbed HF orbitals.

3. Discussion and numerical examples

In this section numerical examples are used to illustrate some of the key problems encountered in property calculations regardless of which method is used to define the uncorrelated reference. We address:

- the question of lack of a variational principle for properties other than energy
- the question of convergence of the perturbation expansion
- the basis set problem, and in particular the different requirements on the basis set for different properties.

No matter what method is used to define the correlation contribution to properties, a key problem encountered is to determine whether or not the computation is converging, and if so if it is to the correct answer. This requires an estimation of the reliability of a property calculated with an approximate wavefunction containing some degree of correlation. In the case of the zeroth-order property, energy, the matter is straightforward. One has the variation principle to guarantee monotonic approach to E_{exact} from E_{HF} as increasing correlation is included in the treatment. In addition, the energy of the Hartree–Fock limit (or a very good approximation to it) is normally available to help with evaluation of basis sets, and a good approximation to E_{exact} is obtainable from experiments for exact comparison to the absolute value of the result.

Neither of these guides is generally available for higher-order properties. As an example, we present in Table 1 a series of Many-Body Perturbation Theory (MBPT) calculations of a first-order property, the dipole moment (μ) of CO [40]. Although the correlation level increases down the table, the value of μ does not vary monotonically with increasing correlation. It is clear that agreement with experiment is a necessary but not sufficient condition for belief that the problem has converged with respect to correlation. In addition, the result must be stable to an increase of the level of correlation. Although these authors get results in good agreement with experiment using a larger basis than that reported here [$10s9p4d2f1g$] and a higher level of correlation (Coupled-Cluster SD(T)), they

Table 1. Dipole moment of CO[a] at different levels of correlation using a $[10s9p4d2f]$ basis

Method	$\mu(D)$
SCF	−0.266
MBPT-2	0.282
MBPT-3	0.047
MBPT-4(D)	0.110
MBPT-4(DQ)	0.071
MBPT-4-(SDQ)	0.118
MBPT-4(SDTQ)	0.235
expt	0.122[b]

[a] From Ref. 40; $R_e = 2.1316$ a.u

[b] Ref. 41

Table 2. Mean excitation energies of He and Be at different levels of correlation

Method		I_0 (eV)
	He[a]	Be[b]
SCF	46.69	32.54
MECI	43.88	36.33
RPA	42.69	42.30
SOPPA	42.41	43.63

[a] $[9s9p5d]$ basis; Ref. 42

[b] $[13s11p4d]$ basis; Ref. 35

comment that the result is neither shown to be converged in basis set nor in the inclusion of correlation.

The effect and importance of added correlation is difficult to generalize among properties and systems. However, we will give a few illustrative examples and attempt to draw some general conclusions therefrom. In Table 2, we present the He and Be mean excitation energy I_0 (derived from the zeroth energy weighted moment of the dipole oscillator strength distribution) calculated using the polarization propagator [35, 42]:

$$\ln I_0 = \sum_{n \neq 0} f_{0n} \ln E_{0n} \Big/ \sum_{n \neq 0} f_{0n} \tag{23}$$

where the $\{f_{0n}\}$ are the dipole oscillator strengths corresponding to the excitations $|0\rangle \rightarrow |n\rangle$ with energy E_{0n}, at various levels of correlation. Although the property varies monotonically with correlation in both cases, the trends are opposite. What is clear in both cases, however, is that inclusion of some correlation is very important (SCF → RPA) while refining the details of correlation (RPA → SOPPA) is not so important. Similar results are obtained for NMR shielding in a variety of systems [9, 43, 44]. The situation is also similar for the first excitation energy and paramagnetic susceptibility of BH [45] as seen in Table 3 and for the first excitation energy in N_2, presented in Table 4. In stark

Table 3. Paramagnetic magnetizability and lowest excitation energy of BH as a function of level of correlation[a]

Method	ξ^p (a.u.)[b]	$\Delta E(X^1\Sigma^+ \rightarrow A^1\Pi)$ (eV)[c]
HF	3.34	4.02
MECI	5.70	2.86
RPA	7.64	2.66
SOPPA	8.05	2.42
CCPPA	6.91	2.90[d,e]

[a] Ref. 45, basis $[9s7p5d2f/7s4p]$

[b] 1 a.u. for ξ, $e^2 a_0^2 m_e^{-1} \simeq 7.89104 \times 10^{-29} JT^{-2}$

[c] At $R_e = 2.336$ a.u

[d] Ref. 46, basis $[8s6p4d/6s3p]$

[e] Experiment [47] 2.87 eV

Table 4. Lowest excitation energy of N_2 as a function of level of correlation

Method	$E(X^1\Sigma^+ \rightarrow w^1\Delta_u)$ (eV)
HF[a]	12.07
MECI[a]	9.23
RPA[a]	8.95
SOPPA[b]	10.54
expt[c]	10.3

[a] Basis 12 of ref. 48; $R_e = 2.068$ a.u

[b] Table 2 of ref. 31

[c] Ref. 47

contrast to these well behaved monotonic cases is the previously mentioned calculation of the dipole moment of CO [40] which responds strongly and erratically to increasing levels of correlation.

Similar properties in the same system often do not exhibit the same trend as a function of the amount of correlation included in the calculation. In Table 5, we present several moments of Quadrupole Oscillator Strength Distribution (QOSD) of N_2 [48]. These moments are second-order properties defined by:

$$S^{(k)}_{\alpha\beta,\gamma\delta} = 2 \sum_{n \neq 0} E_{0n}^{k+1} \langle 0|M_{\alpha\beta}|n\rangle\langle n|M_{\gamma\delta}|0\rangle \tag{24}$$

where the $\{M_{\alpha\beta}\}$ are the Cartesian quadrupole moment operators. It is evident that the effect of correlation is different in different Cartesian directions, and depends on the order of the moment as well. Note that the equivalence of $S(-1)$ in HF and RPA should not be taken as evidence that correlation is not important in this case. It is rather, simply, a consequence of the lack of energy dependence of the property (see Eq. (24)).

Another problem which merits attention is that of basis set. Although no computational basis set is complete, one would like to have a computational basis set which is as complete and balanced as possible. The variation principle assures that adding functions to a basis set will not increase the energy, but gives no help in deciding whether adding tight functions which lower the energy

Table 5. Effect of correlation on the calculation of some moments of the quadrupole oscillator strength distribution[a] in N_2[b]

	HF	MECI	RPA
$S_{x^2,x^2}(0)$	34.4	34.3	29.2
$S_{z^2,z^2}(0)$	109.1	105.6	91.7
$S_{z^2,z^2}(-1)$	77.7	77.7	68.8
$S_{z^2,z^2}(-2)$	37.0	38.2	35.1
$S_{z^2,z^2}(-4)$	114.1	140.0	133.0
$S_{z^2,z^2}(-6)$	226.3	306.6	297.6

[a] In Hartree atomic units

[b] Ref. 48; $R_e = 2.068$ a.u.; Basis $[12s7p2d]$ plus 3 diffuse f-functions at the bond center

Table 6. Effect[a] of basis set and correlation on the $S_{x^2,y^2}(0)$ moment of the quadrupole oscillator strength distribution[b] of N_2

	Basis	$-E_{\text{SCF}}$	$S_{x^2,y^2}(0)$	S_0^L	S_0^V
A	$[12s7p3d]$	108.98940	7.20	13.98	13.76
B	$[12s7p2d]^{c}$	108.98824	7.47	14.11	13.59
C	$[12s7p2d]^{d}$	108.95024	7.23	13.39	12.53
D	$[12s7p2d/3f]^{e}$	108.97120	1.86	13.61	12.87

[a] Ref 48; all quantities in Hartree atomic units; $R_3 = 2.068$ a.u

[b] Calculated at RPA level

[c] Basis A with the most diffuse *d*-function removed

[d] Basis A with the tightest *d*-function removed

[e] Basis C with the three diffuse *f*-function added at bond center

somewhat or very diffuse function which leave the energy unaffected are better for calculation of a specific property, or whether a basis set acceptable at one level of correaltion is good at others as well. In Table 6, we present the $S_{x^2,y^2}(0)$ moments of the QOSD for N_2 at the RPA level [48] for various basis sets. This quantity should be zero in the limit of the exact wavefunction, so the correct answer is known. Although basis *A* gives the best energy, it gives a very poor value of $S_{x^2,y^2}(0)$. This is because the property samples a part of space different than that which is important for the energy.

Other criteria of basis set balance and completeness are, however, available. For example, the Thomax–Reiche–Kuhn sum rule is exact in both its length and velocity forms in RPA in the limit of a complete basis [49]:

$$\begin{aligned} \sum_{n\neq 0} f_{0n}^L &= S_0^L = N \\ \sum_{n\neq 0} f_{0n}^V &= S_0^V = N. \end{aligned} \tag{25}$$

Here *N* is the number of electrons in the system. Satisfaction of the length-velocity equality provides a check on the balance of the basis with regard to tight vs. valence functions, while comparison of the oscillator strength sums with *N* is an indicator of basis set completeness. In Table 6 the calculated values of S_0^L and S_0^V are given for N_2 at the RPA level of correlation for several basis sets. Clearly basis *A* is the best from both the point of view of completeness and balance. Removal of the tightest *d*-function (basis *C*) does considerably more damage to the sum rule and on E_{SCF} than does removal of the most diffuse *d*-function (basis *B*). However, the effect on $S_{x^2,y^2}(0)$ is the opposite. Comparing to our comments concerning $S_{x^2,y^2}(0)$, for which basis *D* is the best, it is clear that different properties require qualitatively different basis sets for proper evaluation.

4. Conclusion

A logical definition of the uncorrelated limit for all order properties, consistent with Löwdin's original definition of correlation energy, is obtained if the same zeroth-order Hamiltonian is used at all orders. To do this consistently implies that the *unperturbed* HF state (that is, with no field included) should be used as the uncorrelated reference. In this case HF/STA is zeroth order and RPA/CPHP is first order and hence correlated.

However, such a choice could be problematical for second- and higher-order properties. One notes that a second-order property $\langle\langle A; B\rangle\rangle_\omega$ is the linear response of the time-dependent quantity $\langle 0(t)|A|0(t)\rangle$, caused by the perturbation operator $B(t)$ [28]. If one then chooses $|0(t)\rangle$ to be the time-dependent HF state (i.e. $|\mathrm{HF}\rangle = |0(-\infty)\rangle$), then one obtains the RPA/CPHF approximation for the linear response function and one might thus argue that RPA is the zeroth-order approximation. Inherent in this line of argumentation is again the assumption that the zeroth-order Hamiltonian (in terms of perturbation theory and not order of the external perturbation) is $H_0 + V(F)$.

Thus, the same result is recovered as from the finite field approach. As the finite field approach and its extensions enjoy growing popularity for calculation of static properties [50], we concede that for second- and higher-order properties, RPA/CHF is a useful and readily accessible standard for comparison, albeit not the most logical choice for the uncorrelated reference for properties and not in accordance with Löwdin's definition for zeroth order properties. The question then becomes not one of inclusion of correlation *per se*, but of inclusion of post-RPA correlation.

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