

Recent Progress in a Green's Function Method for the Calculation of Ionisation Spectra*

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Abstract

The ADC(n) approximation scheme to the one-particle Green function is briefly outlined [ADC(n) stands for algebraic diagrammatic construction accurate to n th order of perturbation theory]. The solution of the equations can be done either by a pole search algorithm (PSA) or by the Davidson diagonalisation approach (DDA) whose problems and advantages are discussed. The results obtained for N₂ are compared. The methods are applied to interpret the ionisation spectra of *p*-quinodimethane, *p*-benzoquinone and to calculate the lowest ionisation energies of the transition metal diatomics Cu₂, Ag₂, Cr₂ and Mo₂. The ADC(4) equations are computationally very demanding and additional approximations need to be introduced in order to apply this method to any but the smallest systems. Such a simplified model is presented and applied to N₂ and CS₂.

1. Introduction

In the study of the electronic structure of atoms, molecules and solids, photoelectron spectroscopy (PES) is a very valuable tool (Siegbahn *et al.* 1967, 1969; Turner *et al.* 1970; Rabalais 1977; Berkowitz 1979; Siegbahn and Karlsson 1982). The classic techniques, i.e. X-ray and ultraviolet photoelectron spectroscopy have been complemented by dipole ($e, 2e$) spectroscopy (Brion and Hamnett 1981) and binary ($e, 2e$) spectroscopy (McCarthy and Weigold 1976; Weigold and McCarthy 1978) and photoelectron spectroscopy using the continuous synchrotron radiation from storage rings (Kunz 1979; Koch 1983). These developments have produced a wealth of data. The single-particle picture or orbital model has been a very useful concept to rationalise this huge amount of data. In the case of closed shell molecules, for example, each line in the spectrum can be associated with an orbital to a first approximation. Molecular vibrations in general broaden these bands. Corrections to this simple picture arise because of electron correlation which is neglected in the self-consistent field (SCF) model. The residual correlation and relaxation effects lead to the appearance of additional weak bands in the photoelectron spectrum; these are called satellite lines.

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The interpretation of photoelectron spectra including satellite lines frequently requires the aid of theoretical calculations. In this respect the Green's function method has been a very valuable tool (Abrikosov *et al.* 1963; Mattuck 1971; Fetter and Walecka 1971; Csanak *et al.* 1971). We consider here this method as it has been developed by Cederbaum and coworkers (Cederbaum 1973, 1975; Cederbaum and Domcke 1977; Schirmer and Cederbaum 1978; Schirmer *et al.* 1983a); for related approaches see Herman *et al.* (1978, 1981), Mishra and Öhrn (1980), Öhrn and Born (1981). In this approach proper account is taken of electronic relaxation and correlation and their effects on the ionisation energies and relative intensities. We discuss here some recent developments, in particular the algebraic diagrammatic construction scheme, ADC(n), which leads to approximations that are accurate to the n th order of perturbation theory and are applicable in the entire energy range (Schirmer *et al.* 1983a). The third order equations, ADC(3), or extended two particle-hole Tamm-Dancoff approximation (extended 2ph-TDA) are solved either by the pole search algorithm (Walter *et al.* 1984) or by the Davidson diagonalisation method (Davidson 1975).

Applications to N_2 , p -quinodimethane, p -benzoquinone and the transition metal diatomics will be given. An approximation to the fourth order equations, ADC(4), is presented which helps to circumvent the excessive numerical demands of the full set of equations. Calculations on N_2 with the full ADC(4) and the approximated version in a restricted orbital basis demonstrate the quality and structure of the results which can be obtained. Comparison with the fourth order model of Baker (1983-5) is made. Finally some preliminary results obtained with the approximated fourth order model on the low energy satellite lines in the photoelectron spectrum of the CS_2 molecule are presented.

2. Outline of the Green's Function Method and the ADC(n) Approximation

The method of Green's function is discussed in general textbooks (Abrikosov *et al.* 1963; Mattuck 1971; Fetter and Walecka 1971) and with a particular emphasis on atomic and molecular physics by Csanak *et al.* (1971). The basic definition is that of the one-particle Green function which is defined with respect to a suitably chosen basis of one-particle states $|p\rangle$ (e.g. Hartree-Fock orbitals) by

$$G_{pq}(t, t') = -i\langle \Psi_0^N | T c_p(t) c_q^\dagger(t') | \Psi_0^N \rangle. \quad (1)$$

Here $|\Psi_0^N\rangle$ is the exact ground state wavefunction of the N -particle system, $c_q^\dagger(t)$ and $c_q(t)$ are the creation and annihilation operators for the states $|q\rangle$ in the Heisenberg representation and T is Wick's time ordering operator which orders the operators so that time increases from left to right. Fourier transforming and inserting the decomposition of unity one obtains the spectral representation

$$G_{pq}(\omega) = \sum_n \frac{\langle \Psi_0^N | c_p | \Psi_n^{N+1} \rangle \langle \Psi_n^{N+1} | c_q^\dagger | \Psi_0^N \rangle}{\omega + A_n} + \sum_m \frac{\langle \Psi_0^N | c_q^\dagger | \Psi_m^{N-1} \rangle \langle \Psi_m^{N-1} | c_p | \Psi_0^N \rangle}{\omega + I_m}, \quad (2)$$

where $A_n = E_0^N - E_n^{N+1}$ is the n th electron affinity and $I_m = E_m^{N-1} - E_0^N$ is the m th ionisation energy. These quantities appear as the poles of the one-particle Green function. The residues are products of the transition amplitudes

$$x_p^{(n)} = \langle \Psi_n^{N-1} | c_p | \Psi_0^N \rangle, \quad (3a)$$

$$y_p^{(n)} = \langle \Psi_n^{N+1} | c_p^\dagger | \Psi_0^N \rangle. \quad (3b)$$

These quantities are related to the spectral intensities of the ionisation and the electron attachment experiment, respectively. In the case of a photoelectron experiment with the photon energy ω_0 sufficiently above the respective threshold for production of ions in the state $|\Psi_n^{N-1}\rangle$, the corresponding partial channel photoionisation cross section is given by the expression

$$\sigma_n(\epsilon) = \frac{2}{3}\epsilon \left| \sum_p \tau_{\epsilon p} x_p^{(n)} \right|^2, \quad (4a)$$

where $\tau_{\epsilon p}$ is the dipole matrix element between the one-particle state $|p\rangle$ and the continuum state $|\epsilon\rangle$ with kinetic energy $\epsilon = \omega_0 - I_n$. The dipole matrix element $\tau_{\epsilon p}$ contains the energy dependence of the cross section, whereas the spectroscopic amplitudes depend only on the electronic properties of the ground and of the parent ionic state. In general, the sum over orbitals p runs over all (occupied and unoccupied) orbitals. Often, however, to a good approximation only one term gives a non-vanishing contribution. Then (4a) simplifies to

$$\sigma_n(\epsilon) = \frac{2}{3}\epsilon |\tau_{\epsilon p}|^2 |x_p^{(n)}|^2. \quad (4b)$$

The pole strength

$$P_n = |x_p^{(n)}|^2 \quad (4c)$$

is called the relative intensity, since it provides a measure for the relative intensities of the states n which derive their intensity from the same orbital p . Of course, this assumes that $|\tau_{\epsilon p}|^2$ is only weakly energy dependent. For a more detailed discussion see Cederbaum and Domcke (1977).

The one-particle Green function matrix G is related to the so-called self-energy matrix Σ by the Dyson equation

$$G(\omega) = G^0(\omega) + G^0(\omega) \Sigma(\omega) G(\omega) \quad (5)$$

or

$$G(\omega)^{-1} = G^0(\omega)^{-1} - \Sigma(\omega), \quad (6)$$

where $G^0(\omega)$ is the Hartree-Fock Green function matrix. The self-energy can be written as the sum of a static part $\Sigma(\infty)$ and a dynamic part $M(\omega)$:

$$\Sigma(\omega) = \Sigma(\infty) + M(\omega), \quad (7)$$

where $M(\omega)$ has the spectral representation

$$M_{pq}(\omega) = \sum_n \frac{m_p^{(n)} m_q^{(n)*}}{\omega - \omega_n} \quad (8)$$

with $m_p^{(n)}$ the coupling (Dyson) amplitudes and ω_n the poles of the self-energy. The M can be decomposed into two parts

$$M(\omega) = M_{(i)}(\omega) + M_{(a)}(\omega) \quad (9)$$

which are analytic in the lower complex plane (i), for ionisation, and the upper complex plane (a), for affinity. They are associated with excitations of $N-1$ and $N+1$ particles, respectively. They do not correspond to energies of physical states which only result upon the coupling to the one-hole (1h) and one-particle (1p) configurations via the Dyson equation. The static self-energy part can be obtained from Green's function according to

$$\sum_{pq}(\infty) = - \sum_{k \in \text{occ}} V_{pk[qk]} + \sum_{kl} V_{pk[ql]} \frac{1}{2\pi i} \oint G_{lk}(\omega) d\omega, \quad (10)$$

with

$$V_{ij[kl]} = V_{ijkl} - V_{ijlk},$$

$$V_{ijkl} = \langle i(1)j(2) | 1/r_{12} | k(1)l(2) \rangle.$$

The contour integration closes in the upper complex ω plane. In summary the calculation of the Green function is reduced to a calculation of the dynamic self-energy $M(\omega)$.

The representation of the self-energy according to equations (7)–(9) allows us to reformulate the Dyson equation (6) as a diagonalisation problem:

$$AX = XE, \quad X^\dagger X = I, \quad (11)$$

$$A = \begin{bmatrix} \epsilon + \Sigma(\infty) & m_{(i)} & m_{(a)} \\ m_{(i)}^\dagger & \Omega_{(i)} & 0 \\ m_{(a)}^\dagger & 0 & \Omega_{(a)} \end{bmatrix}. \quad (12)$$

Here ϵ denotes the diagonal matrix of the orbital energies, $\Omega_{(i, a)}$ are the diagonal matrices of the poles of the self-energy and $m_{(i, a)}$ are the matrices of the corresponding coupling amplitudes. The one-particle Green function is then obtained as

$$G_{pq}(\omega) = \sum_n \frac{x_p^{(n)} x_q^{(n)*}}{\omega - e_n} \quad (13)$$

in terms of the eigenvalues $e_n = E_n$ and eigenvector components $x_p^{(n)} = x_{pn}$.

In the ADC approach it is stated and proved that the exact self-energy $M(\omega)$ [we omit the indices (i) and (a) here as they are unessential to the development] can be

written in the form

$$M_{pq}(\omega) = U_p^\dagger (\omega I - K - C)^{-1} U_q, \quad (14)$$

where U_p is a constant vector of 'modified coupling amplitudes' for the orbital $|p\rangle$ and K and C are constant Hermitian matrices, the latter being referred to as the modified interaction matrix. These quantities are defined with respect to the space of the $(N+1)$ and $(N-1)$ particle excitations excluding the single hole (1h) and single particle (1p) configurations. For $M_{(i)}$ the configurations are given by the 2h-1p, 3h-2p, etc. excitations and for $M_{(a)}$ by the 2p-1h, 3p-2h etc. excitations. The U_p and C matrices are determined by perturbation expansions which start at first order:

$$U_p = U_p^{(1)} + U_p^{(2)} + \dots, \quad C = C^{(1)} + C^{(2)} + \dots \quad (15a, b)$$

The matrix K is a diagonal matrix of orbital energies

$$K_{jkl,jkl} = -\epsilon_j + \epsilon_k + \epsilon_l, \quad K_{ijklm,ijklm} = -\epsilon_i - \epsilon_j + \epsilon_k + \epsilon_l + \epsilon_m, \quad (16)$$

where orbitals i and j are unoccupied and orbitals k, l, m are occupied. A set of systematic approximations $M(\omega; n)$, where $n = 2, 3$, is obtained by requiring that the form

$$M_{pq}(\omega; n) = U_p^\dagger \{ \omega I - K - C(n) \}^{-1} U_q(n) \quad (17)$$

is exact up to n th order in the perturbation, i.e.

$$M_{pq}(\omega; n) = \sum_{v=2}^n M_{pq}^{(v)}(\omega) + O(n+1). \quad (18)$$

This leads to a unique evaluation of the quantities $U_p(n)$ and $C(n)$. The configuration space for the second and third order approximations involves the 2h-1p and 2p-1h configurations, whereas the fourth order approximation involves in addition the 3h-2p and 3p-2h configurations.

The connection with the calculation of the Green function via the Dyson equation can be obtained by observing that the inversion problem of equations (14) or (17) is equivalent to the eigenvalue problem

$$(K + C)Y = Y\Omega. \quad (19)$$

The eigenvalues ω_n determine the poles of the self-energy. The Dyson amplitudes are obtained as

$$m_p^{(n)} = U_p^\dagger Y^{(n)}, \quad (20)$$

where $Y^{(n)}$ is the n th eigenvector. The Dyson equation can then be solved by a diagonalisation according to (11) and (12). This is equivalent, as can easily be seen,

to the following diagonalisation problem:

$$BX = XE, \quad X^\dagger X = I, \tag{21}$$

$$B = \begin{pmatrix} \epsilon + \Sigma(\infty) & U_{(i)}^\dagger & U_{(a)}^\dagger \\ U_{(i)} & K_{(i)} + C_{(i)} & 0 \\ U_{(a)} & 0 & K_{(a)} + C_{(a)} \end{pmatrix}. \tag{22}$$

In the ADC(3) approximation the following equation for *B* is obtained:

$$B = \begin{pmatrix} \epsilon + \Sigma(\infty) & U_{(i)}^{I\dagger} & U_{(a)}^{I\dagger} \\ U_{(i)}^I & K_{(i)}^I + C_{(i)}^I & 0 \\ U_{(a)}^I & 0 & K_{(a)}^I + C_{(a)}^I \end{pmatrix}, \tag{23}$$

where I denotes the space of 2h–1p or 2p–1h configurations. In fourth order, the *B* matrix given pictorially in Fig. 1 results, where II denotes the space of 3h–2p or 3p–2h configurations. The equations derived in this way are of quite general applicability, i.e. the ADC(*n*) scheme can be applied in the entire energy region as the important property of the self-energy poles as being simple poles is maintained throughout. A simple perturbation expansion of the self-energy, as is done in the outer-valence Green’s function method (OVGF) (Cederbaum 1973, 1975; Cederbaum and Domcke 1977), can only be used far away from the poles of the self-energy and is thus of restricted applicability.

	1h/1p	2h-1p	3h-2p	2p-1h	3p-2h
1h/1p	$\epsilon + \Sigma^{(4)}(\infty)$	$U_{(i)}^I + E$	$U_{(i)}^{II} \equiv D$	$U_{(a)}^I + E'$	$U_{(a)}^{II} \equiv D'$
2h-1p		$(K_{(i)} + C_{(i)})^I + A$	$C_{(i)}^{(I, II)}$	0	0
3h-2p			$(K_{(i)} + C_{(i)})^{II} \equiv B$	0	0
2p-1h				$(K_{(a)} + C_{(a)})^I + A'$	$C_{(a)}^{(I, II)}$
3p-2h					$(K_{(a)} + C_{(a)})^{II} \equiv B'$

Fig. 1. The ADC(4) matrix for the Green function shown schematically. The third order matrices are denoted as *X*^I while the additional fourth order matrices are denoted as *Y*^{II}. The fourth order contributions to the *X*^I blocks are shown separately in each *X*^I block. The index (I, II) refers to the coupling between 2h–1p and 3h–2p spaces (2p–1h and 3p–2h, respectively).

The structure of the matrix *B* in the third and fourth order approximation appears to be very similar but a few things should be noted which affect strongly the computational feasibility of the two approaches. Because of the appearance of the 3h–2p and 3p–2h configurations in the ADC(4) scheme, the dimension of the matrices is increased by one to two orders of magnitude. Whereas in the ADC(3) approach the *U* matrices contain linear and quadratic terms in the Coulomb matrix elements *V*_{*ijkl*} and the *C* matrices only linear terms, the ADC(4) scheme introduces cubic

terms in V_{ijkl} (denoted as E in Fig. 1) and quadratic terms (denoted as A in Fig. 1). It is obvious that the ADC(4) calculations will be very demanding and additional approximations will have to be introduced if one wishes to compute more than only the lowest energy ionisations.

Two technical realisations can be envisaged by considering, on the one hand, equations (11) and (12), where the m and Ω matrices result from the diagonalisation of equations (19) and (20) and, on the other hand, equations (21) and (22). The matrix A of equation (12) has a particular 'arrow' type form. Matrices of such a type can be diagonalised by the pole search algorithm of Walter *et al.* (1984) for dimensions up to about 10^4 . Moreover this algorithm permits one to obtain all eigenvalues and eigenvectors in a preset energy interval, which is an ideal situation. A prerequisite is, however, the complete diagonalisation according to equation (19) which yields the poles of the self-energy and the Dyson amplitudes. Such complete diagonalisations can be performed up to dimensions of a few hundred (let us say 600 to give a reasonable value). The dimension of the matrices, however, is equal to the number of $2h-1p$ (or $2p-1h$) configurations which can be many thousand. Consequently only a restricted number of configurations can be taken into account fully, the remaining configurations are taken into account in a diagonal approximation. This leads to the problem of configuration selection (von Niessen *et al.* 1984). This approach turned out to be quite successful.

The alternative to this pole search algorithm is to diagonalise the matrix of equation (22) directly by an algorithm developed for large matrices, for example, the Davidson (1975) method. This has been advocated in the framework of the Green's function method by Baker (1983-5). In this way many more configurations can be taken into account but there is no systematic way to obtain all eigenvalues in a preset interval. It turns out that the Davidson diagonalisation method can be successfully employed if the density of states is low, but it is not very helpful if the density of states is very high. A disadvantage of this method is also that the static self-energy must be diagrammatically evaluated. An analysis by Schirmer *et al.* (1983*a*) has shown that if $\Sigma(\infty)$ is evaluated self-consistently from the Green function it is exact to fourth order already in the ADC(3) approach. A diagrammatic expansion of $\Sigma(\infty)$ starts at third order. In the ADC(3) approach one would include normally only terms up to this order, because the fourth order terms are very expensive again. This may strongly affect the results as will be discussed below.

3. Application of the ADC(3) Method to N_2

The complex inner-valence-shell ionisation spectra of molecules, including the study of satellite lines, form an important subject of present day experimental and theoretical investigations. Recently, new experimental data have been reported for N_2 obtained by synchrotron radiation (Krummacher *et al.* 1980). This has corroborated previous experimental work (for references to these see Krummacher *et al.*). An extended structure of numerous peaks is found in the region of 25-45 eV binding energy, which cannot be explained by the single-particle picture of ionisation. Due to strong configuration mixing between the inner-valence hole configuration and $2h-1p$ configurations, a multitude of final ionic states results which shares the partial ionisation cross section for the respective inner-valence orbital. Theoretical calculations for N_2 and CO have documented that this is the case (Bagus and

Viinikka 1977; Schirmer *et al.* 1977; Herman *et al.* 1978; Langhoff *et al.* 1981). This failure of the single-particle picture of ionisation was found to be a common phenomenon (for references and a survey see von Niessen *et al.* 1984; Cederbaum *et al.* 1986). The objective of this section is to provide applications of the ADC(3) method in the two implementations involving the pole search algorithm (PSA) and the Davidson diagonalisation approach (DDA). The ADC(3) results have been published by Schirmer *et al.* (1983*b*). The SCF calculations on N₂ were performed at an internuclear separation of 2.0693 a.u. with the [11s7p1d]/(5s4p1d) basis set of Salez and Veillard (1968). In both calculations 42 orbitals were included and only the core orbitals and their high energy virtual counterparts were neglected. The 2h–1p space has a maximum dimension of 146 and the 2p–1h space of 1028. In the latter case configuration selection had to be used including the remaining configurations which were not selected in a diagonal approximation. From the calculations it emerged that 400 selected configurations were sufficient; increasing this number to 600 resulted in no significant change in the energies.

Table 1. Vertical ionisation energies I_n (eV) and pole strengths P_n of N₂ obtained from the ADC(3) approximation with the PSA and DDA

Only states with a pole strength exceeding 0.01 are listed

Symmetry	ADC(3) (PSA)			ADC(3) (DDA)			OVGF ^A	Exp.
	I_n	P_1	P_2	I_n	P_1	P_2		
$^2\Sigma_g^+$	15.70	0	0.91	15.48		0.91	15.44	
	29.20	0.10		29.16	0.11	0.014		15.6 ^B
	37.43	0.30		37.32	0.41			29.4 ^C
	37.56	0.10		37.54	0.03			(35.0
	38.97	0.14		38.93	0.14			
	39.25	0.04		39.24	0.027			
	39.94	0.15		39.90	0.13			
	40.62	0.06		40.61	0.044			40.0 ^C
$^2\Sigma_u^+$	18.96	0.82		18.78	0.82		18.89	18.8 ^B
	25.13	0.07		25.12	0.07			25.2 ^D
	35.34	0.02		35.34	0.024			
$^2\Pi_u$	16.85	0.92		16.62	0.92		16.74	17.0 ^B

^A von Niessen *et al.* (1977, 1984).
^B Turner *et al.* (1970).
^C Krummacher *et al.* (1980).
^D Åsbrink and Fridh (1974) and Åsbrink *et al.* (1974).

The results for N₂ obtained in the PSA and DDA implementations are listed in Table 1 which also contains the results from the OVGF and the experimental values. The agreement between the two ADC(3) calculations is very close, in particular with respect to the energies of the satellite lines. The greater discrepancy found for the main lines is essentially due to the treatment of the $\Sigma(\infty)$ terms.

A significant redistribution of the intensities occurs only for the two states above 37 eV. They are closer together in the PSA calculation (separation 0.13 eV) than in the DDA calculation (0.22 eV) which explains the more even intensity distribution in the PSA compared with the DDA calculation. We thus note the great sensitivity of the intensity of the lines in the case of a close separation. It is apparent from Table 1 that the DDA calculation has been able to find all solutions in the energy

region investigated. The agreement of the two sets of results with the OVGf results is also very close.

4. Application to *p*-Quinodimethane (PQDM) and *p*-Benzoquinone (PBQ)

We selected these two molecules for a number of reasons. The very low energy satellite lines found for PQDM have been of considerable interest recently, and the assignment of the photoelectron spectrum for PBQ is of continuing interest. From a technical point of view the molecules are large, and in the ADC(3) PSA calculation the basis set cannot be exhausted, but this is (nearly) possible in the ADC(3) DDA and OVGf calculations. On the other hand, the density of states is very high and the DDA method can hardly be used to obtain all ionisation energies. We thus require all these different methods to study these molecules.

Satellite lines are very abundant in photoelectron spectra. It is not surprising that in larger organic molecules satellite lines appear at very low energies. In 1975 Koenig and coworkers assigned a weak feature in the PES of PQDM to a satellite line. Their interpretation was not universally accepted (Dewar 1982), but a considerable amount of research both by spectroscopy and by theoretical calculations established that their original interpretation is most likely the correct one (Koenig *et al.* 1975, 1983; Koenig and Southworth 1977; Schulz *et al.* 1983; Bigelow 1983; Ha 1984). Since this time, the search for low energy satellite lines is a very active field of research.

We have applied the ADC(3) method to PQDM, employing a double-zeta basis set in the calculations. The ionisation spectrum calculated with this method in the entire valence region is shown in Fig. 2 which also contains the PES from Koenig *et al.* (1975). From the spectrum we conclude that the one-particle model of ionisation applies only to ionisation from the orbitals $2b_{3u}(\pi)$, $1b_{1g}(\pi)$, $3b_{3g}$, $5a_g$, $4b_{2u}$, $4b_{1u}$, $2b_{3g}$, $3b_{2u}$ and $2b_{2u}$ but not to ionisation from some of the lowest binding energy orbitals $18 = 1b_{2g}(\pi)$ and $16 = 1b_{3u}(\pi)$, although appreciable satellite line structure is also found for the other cases. According to the ADC(3) calculation, the $1b_{2g}$ line is split into two strong components and one weaker component. The first component is calculated to lie at slightly lower energy than the $1b_{1g}$ line and the second component slightly before the $3b_{3g}$ line. All semi-empirical and *ab initio* calculations agree that the two components contribute to the second and third band systems in the PES.

The configurations which contribute dominantly to the line are $1b_{2g}^{-1}$, $2b_{3u}^{-2}$ $2b_{2g}$ and somewhat less $1b_{1g}^{-1}$ $2b_{3u}^{-1}$ $1a_u$. The first two configurations contribute to both components of the line with about equal weight and no line can be called the main line and the other one the satellite line.

The second low energy line which splits is the $1b_{3u}(\pi)$ line. Here we obtain again two strong components and one somewhat weaker component (Fig. 2). The first component contributes to the fourth band system ($5a_g$ and $4b_{2u}$ ionisation) and the second component to the fifth band system ($4b_{1u}$ and $2b_{3g}$ ionisation). The dominant configurations are in this case $1b_{3u}^{-1}$ and $2b_{3u}^{-2}$ $3b_{3u}$ and with somewhat smaller weight $1b_{2g}^{-1}$ $2b_{3u}^{-1}$ $2b_{2g}$ and $1b_{2g}^{-1}$ $1b_{1g}^{-1}$ $1a_u$. Thus the dominant excitation process is in this case not the HOMO-LUMO excitation but the excitation from the HOMO into a higher lying virtual orbital.

Above about 16 eV a very dense structure of lines is found, typical for the complete breakdown of the molecular orbital model of ionisation. This structure can only be considered as qualitatively correct.

Fig. 2. Ionisation spectrum of *p*-quinodimethane as obtained by the ADC(3) PSA method. The experimental spectrum is from Koenig *et al.* (1975).

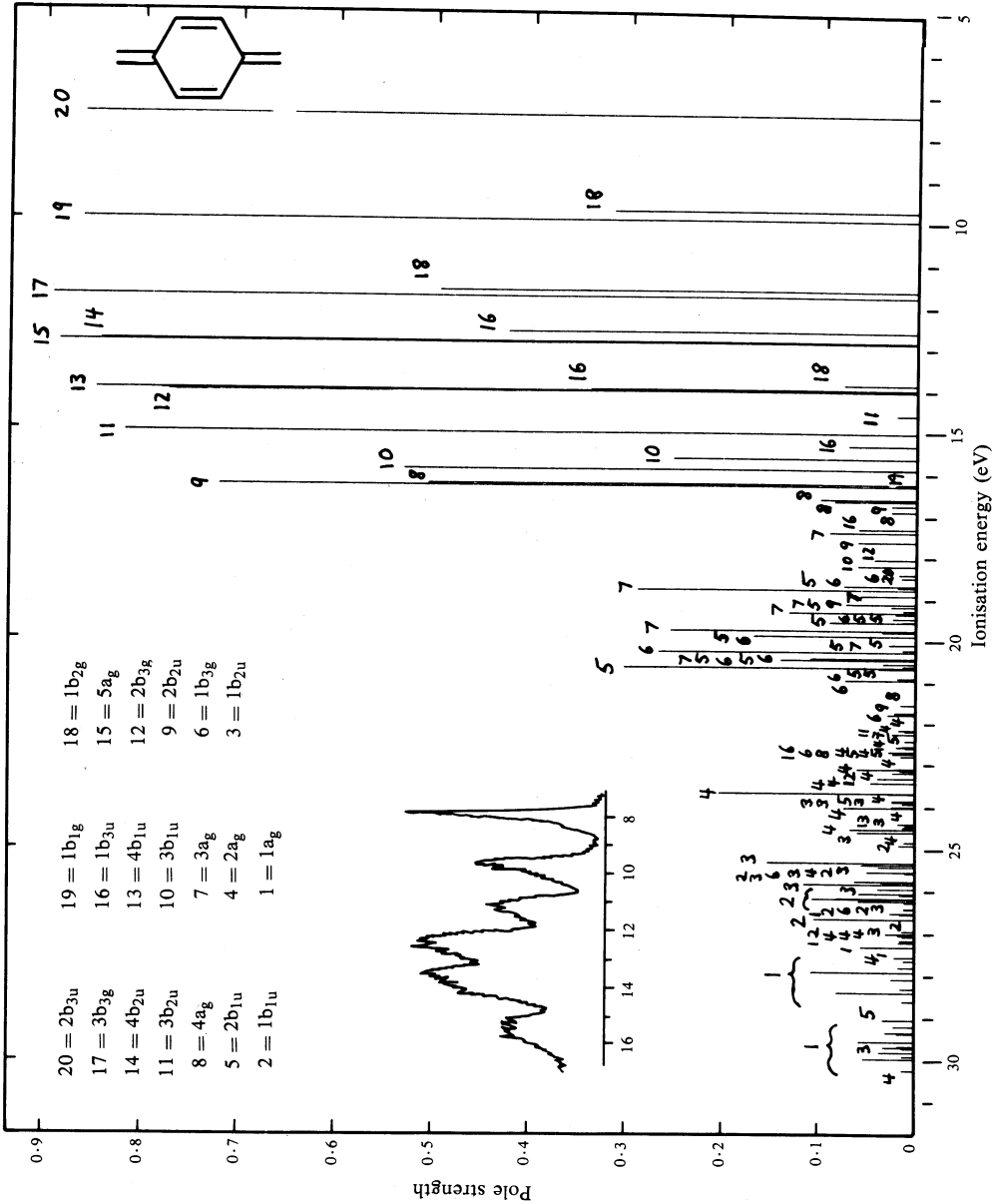


Table 2. Lowest ionisation energies (eV) of *p*-quinodimethane
Pole strengths are in parentheses

Symmetry	$-\epsilon_i$	OVGF	ADC(3) PSA ^A	ADC(3) DDA ^A	Exp. ^B
2b _{3u}	7.36	7.31 (0.89)	7.46 (0.86)	7.35 (0.86)	7.87
1b _{2g}			9.72 (0.32)	9.33 (0.22)	9.7
1b _{1g}	10.24	9.71 (0.89)	9.95 (0.86)	9.75 (0.87)	9.8
1b _{2g}	11.41		11.63 (0.50)	11.12 (0.58)	11.1
3b _{3g}	13.04	11.44 (0.90)	11.77 (0.89)	11.56 (0.89)	
1b _{3u}	14.30		12.60 (0.42)		(12.2
5a _g	14.35	12.45 (0.90)	12.87 (0.89)	12.57 (0.89)	
4b _{2u}	14.46	12.65 (0.88)	12.84 (0.84)	12.70 (0.85)	12.8)
1b _{2g}			13.85 (0.076)		
1b _{3u}			13.99 (0.34)		(13.6
4b _{1u}	15.68	13.72 (0.89)	14.00 (0.85)	13.79 (0.85)	
2b _{3g}	15.80	13.96 (0.86)	14.01 (0.78)		
3b _{2u}			14.59 (0.021)		14.3)
3b _{2u}	16.61	14.70 (0.88)	15.01 (0.82)		(15.2
1b _{3u}			15.31 (0.071)		
3b _{1u}			15.63 (0.25)		
3b _{1u}	17.58		15.89 (0.53)		
4a _g	18.46		16.23 (0.51)		
1b _{1g}			16.24 (0.019)		16.0)
2b _{2u}	18.44		16.27 (0.72)		
4a _g			16.60 (0.10)		
4a _g			16.65 (0.085)		

^A Note that a different number of orbitals and configurations are included in each of these columns.

^B From Koenig *et al.* (1975).

In Table 2 we have summarised the lowest ionisation energies of PQDM and compared them with the experimental values. We note that the ADC(3) PSA calculation involves a smaller number of orbitals and configurations than the other calculations. The ADC(3) DDA results are in very good agreement with the OVGF results as far as this method can be applied (validity of the single-particle picture of ionisation). The ADC(3) PSA results are higher in energy than the ADC(3) DDA results because of the inclusion of more orbitals and more configurations in the latter calculation which leads to a more complete account of relaxation effects. The agreement with experiment is as satisfactory as can be expected from the use of a double-zeta basis.

The assignment of the first four bands of PBQ has for a long time been a hotly debated problem (Cowan *et al.* 1971; Brundle *et al.* 1971; Lauer *et al.* 1975; Kobayashi 1975; Wood 1975; Dougherty and McGlynn 1977; Bigelow 1978; Bloor *et al.* 1979; Åsbrink *et al.* 1979; Jacques *et al.* 1981; Ha 1983; for a discussion and detailed references see von Niessen *et al.* 1986). The two lowest energy π ionisations 2b_{3u}(π_+) and 1b_{1g}(π_-) and the two oxygen lone pair orbitals 3b_{3g}(n_+) and 4b_{2u}(n_-) are to be found in an interval barely exceeding 1 eV. The two most probable orderings listed with increasing binding energy are n_+ , n_- , π_+ , π_- and n_+ , π_+ , n_- , π_- , where the first ordering is now preferred. The assignment is of particular interest since Koopmans' approximation predicts the ordering π , π , n , n , with a substantial energy gap between the π and the n orbitals. But we expect that the n -ionisation energies

will be shifted more strongly to lower energies compared with the π energies. Such a behaviour is indeed found and we observe a double interchange of both n -ionisation energies with both π energies.

In Table 3 the lowest ionisation energies obtained with the OVGf, the ADC(3) PSA and the ADC(3) DDA methods are listed, together with the available experimental

Table 3. Lowest ionisation energies (eV) of *p*-benzoquinone
Pole strengths are in parentheses

Symmetry	$-\epsilon_i$	OVGF	ADC(3) PSA ^A	ADC(3) DDA ^A	Exp. ^B	Exp. ^C
3b _{3g} (n_+)	12.35	10.19 (0.89)	10.49 (0.83)	10.18 (0.82)	10.11	9.99
4b _{2u} (n_-)	13.01	10.65 (0.87)	10.87 (0.80)	10.71 (0.81)	10.41	10.29
2b _{3u} (π_+)	11.31	10.74 (0.89)	10.73 (0.84)	10.75 (0.85)	11.06	10.93
1b _{1g} (π_-)	11.56	10.82 (0.91)	11.31 (0.88)	10.89 (0.90)	11.25	11.0
1b _{2g}	15.31		13.02 (0.37)	12.92 (0.27)	$\sim 13^D$	
2b _{3g}	16.27		13.91 (0.59)		13.43	13.5
2b _{3g}			14.17 (0.19)			
5a _g	16.49	14.43 (0.90)	14.49 (0.84)	14.38 (0.59)	14.38	14.3
1b _{3u}	16.61		14.80 (0.63)		14.54	14.8
5a _g			14.95 (0.015)			
1b _{2g}			14.96 (0.32)	14.72 (0.42)	15.05	14.9
4b _{1u}			15.02 (0.059)			
4b _{1u}	17.32		15.16 (0.76)	15.03 (0.71)	15.30	15.0
3b _{2u}	17.85	15.76 (0.89)	15.75 (0.85)		15.50	15.5
2b _{2u} + 4b _{2u}			16.40 (0.22)			16.2
3b _{1u}	18.66	16.45 (0.87)	16.42 (0.80)		16.46	16.7
2b _{2u}			16.50 (0.028)			
1b _{2g}			16.78 (0.055)			
2b _{3g} + 3b _{3g}			16.95 (0.12)			
4a _g	19.53		16.99 (0.75)		16.92	17.0
2b _{2u}			17.15 (0.031)			
2b _{2u}	20.02		17.71 (0.54)			
3b _{1u}			18.02 (0.021)			
1b _{2g}			18.16 (0.074)			
2b _{2u}			18.18 (0.020)			
1b _{3u}			18.40 (0.21)			
2b _{2u}			18.43 (0.017)			
4a _g			18.54 (0.035)			
2b _{2u}			19.16 (0.023)			
1b _{3u}			19.19 (0.041)			
2b _{3g}			19.33 (0.020)			
2b _{2u}			19.50 (0.015)			
1b _{2g}			19.51 (0.028)			
3a _g	23.05		19.66 (0.31)			19.5
3a _g			19.85 (0.17)			
2b _{2u}			20.06 (0.025)			
3b _{1u}			20.37 (0.045)			
1b _{3g}	23.99		20.85 (0.54)			20.1

^A Note that a different number of orbitals and configurations are included in each of these columns.

^B From Turner *et al.* (1970).

^C From Åsbrink *et al.* (1979).

^D See text.

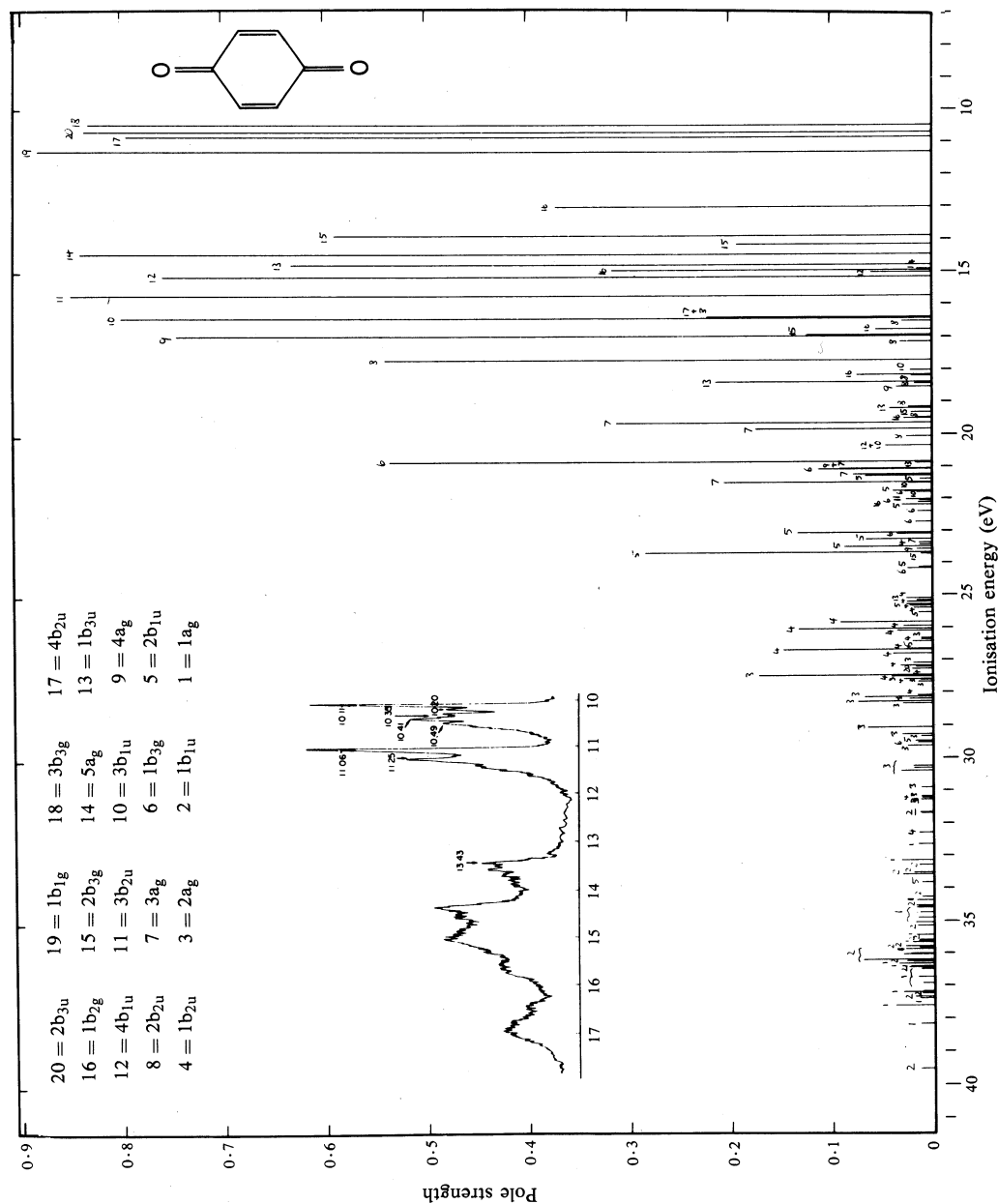


Fig. 3. Ionisation spectrum of *p*-benzoquinone as obtained by the ADC(3) PSA method. The experimental spectrum is from Turner *et al.* (1970). The assignments of the second and third states here differ from those of the more reliable calculations in the present work because of restricted orbital space in the PSA calculation (see text).

results. The ionisation spectrum computed by the ADC(3) PSA method is plotted in Fig. 3, which also contains the PES from Turner *et al.* (1970) as an insert. One notes that the first four bands have a different ordering in the calculations. The OVGF and the ADC(3) DDA calculations which both completely exhaust the basis set give the ordering $3b_{3g}(n_+)$, $4b_{2u}(n_-)$, $2b_{3u}(\pi_+)$, $1b_{1g}(\pi_-)$ which is the preferred one, whereas the ADC(3) PSA calculation which does not exhaust the basis gives an inversion of the n_- and π_+ states. The configuration expansion thus has to be fairly complete in the given basis set in the present case. The first two calculations are more reliable and we accept the ordering n_+ , n_- , π_+ , π_- as the correct one in our model. However, we do not consider the problem settled since some of the calculated vertical ionisation energies are very close together. None of the calculational methods (*ab initio* or semi-empirical) has for such a relatively large molecule the accuracy of less than 0.2 eV to unambiguously resolve the assignment problem. Besides, the small separation of the bands may give rise to vibronic coupling.

We see from Fig. 3 that out of the twenty valence orbitals nine are associated with main lines having large pole strengths. The four orbitals $2b_{3g}$, $1b_{3u}(\pi)$, $2b_{2u}$ and $1b_{3g}$ are taking an intermediate position. They have pole strengths from about 0.5 to 0.6. All other orbitals are subject to severe final state correlation effects. In the experimental spectrum, the next band following the closely spaced first four ionisations appears at 13.43 eV, but around 13 eV some weak structure can be seen. Actually this is not noise as it appears reproducibly in all spectra. In this energy range we calculate the first strong component of $1b_{2g}$ ionisation which has become split into two strong components and a number of weaker components. The first two strong components are separated by about 2 eV showing that strong many-body effects are active. We cannot definitely decide whether the first component of $1b_{2g}$ ionisation lies within the band at 13.43 eV or is to be assigned to the noise around 13 eV as the calculations are not accurate enough. That a broader band may result upon $1b_{2g}$ ionisation is understandable. The $1b_{2g}$ orbital is C=O bonding and, in addition, the $1b_{2g}^{-1}$ configuration mixes with the $2b_{3u}^{-2} 2b_{2g}$ configuration which involves an excitation from a bonding to an antibonding orbital. Hence the bonds become considerably weakened which may result in a very extended vibrational progression. Explicit calculations are needed to support this speculation. As seen from Fig. 3, the orbitals from 16 to 8 contribute to the extended band system between 13 and 18 eV binding energy. A one-to-one assignment is difficult because of the close spacing of the bands, the splitting of the lines and appearance of satellite lines. A tentative assignment is incorporated into Table 3. Beyond approximately 18 eV binding energy, the computed spectrum exhibits numerous lines emerging mainly from the ionisation of the inner valence orbitals. The orbital picture of ionisation loses completely its significance.

5. Ionisation Energies of the Transition Metal Diatomics Cu_2 , Ag_2 , Cr_2 , Mo_2

The transition metal diatomics have over the past few years received considerable attention from experiment and theory (for references see von Niessen 1986). The experimental techniques to study these highly reactive species have been greatly improved and resulted in very valuable information. Bond distances, bond energies, the ground and the lowest excited states have been studied. However, due to the high energy required and the great experimental difficulties, little information is available

on the ionisation energies. A very precise value has been measured for Cu_2 (Powers *et al.* 1983), a value with large error bounds exists for Ag_2 (Cocke and Gingerich 1971) and an upper limit for the ionisation energy of Mo_2 has been determined (Hopkins *et al.* 1983). No information is given in the literature regarding Cr_2 . The theoretical methods which aim at the inclusion of the correlation energy are in some cases in great difficulties in describing the electronic structure properly. The difficulties arise from the large number of electrons to be correlated and from the fact that in some cases (e.g. for Cr_2) the Hartree-Fock configuration contributes only a few per cent to the ground state wavefunction and a many-reference configuration wavefunction is the first meaningful approximation. Thus for Cr_2 the *ab initio* configuration interaction (CI) methods predict a long, weak bond in contrast to experiment.

We have applied the OVGf and the ADC(3) methods to the calculation of the ionisation energies of Cu_2 , Ag_2 , Cr_2 and Mo_2 . The basis sets are taken from the work of Huzinaga (1977) and have been enlarged somewhat by Hay (1977). The Cu_2 and Ag_2 molecules have the electronic configuration $1\sigma_g^2 1\pi_u^4 1\delta_g^4 1\delta_u^4 1\pi_g^4 1\sigma_u^2 2\sigma_g^2 (^1\Sigma_g^+)$ in their ground state corresponding to a completely filled d shell ($3d^{10}4s^1$ for Cu and $4d^{10}5s^1$ for Ag). The Cr_2 and Mo_2 molecules in their ground state have the electronic configuration $1\sigma_g^2 1\pi_u^4 1\delta_g^4 2\sigma_g^2 (^1\Sigma_g^+)$ corresponding to a half filled d shell. But as mentioned above, the HF wavefunction contributes only a little to the total wavefunction. From the calculations, the following points emerged. The OVGf method can only be applied to the lowest ionisation energy of Cu_2 and Ag_2 (i.e. the $2\sigma_g$ orbital which is essentially formed from the 4s or 5s orbitals, respectively). In the other cases, poles of the self-energy invalidate the use of the OVGf method. Moreover, it is found that the static self-energy terms tend to 'diverge' in third order. For Cr_2 they are of the order of 40–50 eV, whereas normally they are 1–3 eV. If the ADC(3) PSA method is used in which these terms are calculated accurately to fourth order, they are again of the order of 1 eV. Since the static self-energy terms are essentially ground state energy terms, it is seen that a third order approximation is for some terms an inappropriate approximation for the transition metal diatomics. This behaviour of the static self-energy also renders the ADC(3) DDA method inapplicable except for the lowest ionisation energies of Cu_2 and Ag_2 .

Table 4. Calculated and experimental lowest ionisation energies (eV) of Cu_2 , Ag_2 , Cr_2 and Mo_2

Molecule	OVGF	ADC(3) PSA	ADC(3) DDA	Exp.
Cu_2	7.76	7.06	7.78	7.894 ^A
Ag_2	6.75	6.56	6.70	6.4 ± 0.7 ^B
Cr_2	—	6.76	—	—
Mo_2	—	6.21	—	< 6.42 ^C

^A From Powers *et al.* (1983).

^B From Cocke and Gingerich (1971).

^C From Hopkins *et al.* (1983).

In Table 4 we list the theoretical and experimental values for the lowest ionisation energies of Cu_2 , Ag_2 , Cr_2 and Mo_2 . The agreement between the OVGf and the ADC(3) DDA results is again very good. The greater discrepancy found for Cu_2 with the ADC(3) PSA method is due to the lack of exhaustion of the basis set. The agreement obtained with experiment is also very satisfactory. It should be noted

that in particular the result for Cr_2 should be viewed with some caution as the HF wavefunction does not properly describe the ground state of this molecule and the Green's function method in its present form assumes that this is the case.

6. Proposed Simplification of the ADC(4) Scheme

As the analysis of Schirmer *et al.* (1983*a*) has shown, the energies of the main ionic states are described accurately to third order by the ADC(3) scheme, whereas the satellite lines which are dominated by 2h-1p configurations are only described correctly to first order. If one is interested in the energies of the satellite lines and if one encounters the breakdown of the molecular orbital model of ionisation this is insufficient. A higher order approximation such as ADC(4) is desirable. It should, however, be pointed out that basis sets also pose severe problems. In the neighbourhood of the double ionisation threshold which usually lies in the region of interest, an infinity of Rydberg states of the ion is found which would require an infinite basis for their calculation. Thus quantitative results in this region are out of range. The ADC(4) method describes the main ionic states accurately to fourth order and the satellite lines accurately to second order of perturbation. As the ADC(3) method is already quite accurate for the main ionic states we principally aim at an improvement in the satellite lines. The computational expense of the full ADC(4) equations is very large in two respects: the dimension of the matrices which increases by one to two orders of magnitude and the complicated matrix elements which arise in fourth order. We refer to Fig. 1, where particularly cumbersome are the large 3h-2p and 3p-2h spaces and the E, E' matrix elements which are cubic in the V_{ijkl} matrix elements.

In order to assess the importance of the individual fourth order terms, a number of calculations were done on the N_2 molecule in two different basis sets: the [9s5p]/(3s2p) basis (Huzinaga 1965) and the extended [11s7p1d]/(5s4p1d) basis set of Salez and Veillard (1968). The calculations (Tomasello *et al.* 1986) lead to the following conclusions which, however, should be ascertained by more extended and diversified applications: The terms A and A' (see Fig. 1) in general act in opposite directions as do the terms E and E' and the effect of the combined terms A, A' is opposite to that of the combined E, E' terms. This is typical for the Green's function method. The A' term is negligible compared with A for ionisation processes. The A term must be included; its effect on the main ionic states is about 0.1 eV but the satellite lines are very strongly affected as is expected. The terms E and E' should either both be neglected or both be included. Their effect on the main ionisation energies is basis set dependent. In the double-zeta basis set, the effects amount to maximally 0.2-0.3 eV; in the extended basis the effects are negligible. The satellite lines remain nearly unaffected by these terms. Since the E, E' terms are computationally very expensive and since we aim at an improved description of the satellite lines we tend to neglect them. The large $B'(3p-2h)$ matrix is of little relevance to the ionisation energies. Satellite lines are nearly unaffected and the ionic main states may experience maximum shifts of about 0.1 eV. The large $B(3h-2p)$ matrix on the other hand needs to be included even if configuration selection has to be used, since many new poles arise as a result and lead to an improved representation of the self-energy. It is, however, not meaningful to use the zeroth order approximation to B , i.e. a diagonal matrix of orbital energies as done by Baker (1984, 1985). Such an approximation changes

	1h/1p	2h-1p	3h-2p	2p-1h
1h/1p	$\epsilon + \Sigma^{(4)}(\infty)$	$U_{(i)}^I$	$U_{(i)}^{II}$	$U_{(a)}^I$
2h-1p		$(K_{(i)} + C_{(i)})^I + A$	$C_{(i)}^{(I, II)}$	0
3h-2p			$(K_{(i)} + C_{(i)})^{II}$	0
2p-1h				$(K_{(a)} + C_{(a)})^I$

Fig. 4. Matrix of the proposed simplified ADC(4) model.

	1h/1p	2h-1p	3h-2p	2p-1h
1h/1p	$\epsilon + \Sigma^{(3)}(\infty)$	$U_{(i)}^I$	0	$U_{(a)}^I$
2h-1p		$(K_{(i)} + C_{(i)})^I$	$C_{(i)}^{(I, II)}$	0
3h-2p			$K_{(i)}^{II}$	0
2p-1h				$(K_{(a)} + C_{(a)})^I$

Fig. 5. Matrix of the model proposed by Baker including some fourth order terms (Baker 1984, 1985).

qualitatively the structure of the satellite lines. We thus arrive at the following simplified ADC(4) scheme which is computationally tractable and still preserves the main effects coming from the fourth order treatment. The model is represented in Fig. 4. We neglect all the fourth order terms of the affinity part of the self-energy (i.e. A', B', C', D', E') and the E term of the ionisation part. This model retains more terms than the model suggested by Baker (1984, 1985) which is represented in Fig. 5. Baker has, in addition, omitted the term $U_{(i)}^{II}$ of Fig. 4 (which according to our calculation on N_2 may be omitted, but we included it since it causes no computational problems), the term A , which definitely should not be left out, and he used the zeroth order approximation to the 3h-2p block which is also inappropriate according to our experience. For N_2 and the case of the double-zeta basis set, we compare in Table 5 the results obtained with the proposed simplified ADC(4) model [here denoted as ADC(3.5)] and with the complete ADC(4) approximation. The agreement can be considered as very satisfactory.

In order to compare with experiment and with the POLCI calculations of Langhoff *et al.* (1981), a calculation was done on N_2 with an extended basis set. In the third order terms, 33 virtual orbitals (out of 37 valence-like virtual orbitals) were included, and in the fourth order terms 11 virtual orbitals were included. In the POLCI calculation, selected 3h-2p configurations were included in addition to the configurations of a single excitation wavefunction (SECI), but a restriction was made

in the double excitations in that at least one electron had to involve the $1\pi_g$ orbital. This $1\pi_g$ orbital was not taken from the ground state calculation on N_2 but from a SCF calculation on the $(3\sigma_g \rightarrow 1\pi_g)^1\Pi_g$ excited state in order to obtain a more compact $1\pi_g$ orbital.

Table 5. The ADC(4) ionisation energies (eV) for N_2 in a double-zeta basis
Pole strengths (in parentheses). They refer to the contributions from the $2\sigma_g$ and $3\sigma_g$ orbitals for σ_g symmetry

ADC(3.5) ^A			ADC(4) ^B		
	$2\sigma_g$	$3\sigma_g$		$2\sigma_g$	$3\sigma_g$
14.09	—	(0.899)	14.04	—	(0.890)
27.41	(0.06)	(0.016)	27.43	(0.055)	(0.029)
30.76	(0.030)	(0.002)	30.76	(0.032)	(0.003)
34.14	(0.005)	(0.006)	34.15	(0.009)	(0.008)
35.95	(0.002)	(0.001)	35.95	(0.003)	(0.002)
38.34	(0.303)	—	38.32	(0.281)	—
39.94	(0.03)	—	38.95	(0.030)	—
39.80	(0.22)	—	39.79	(0.21)	—
40.35	(0.12)	—	40.40	(0.14)	—
41.92	(0.03)	—	41.94	(0.06)	—
$1\pi_u$					
16.63	(0.918)		16.81	(0.91)	
26.93	—		26.93	—	
29.83	(0.01)		29.83	(0.01)	
31.02	(0.001)		31.01	(0.001)	
32.70	—		32.70	—	
34.67	—		34.67	—	
37.04	—		37.04	—	
37.30	—		37.30	—	
$2\sigma_u$					
17.45	(0.811)		17.23	(0.81)	
24.33	(0.075)		24.30	(0.07)	
32.63	(0.039)		32.79	(0.05)	
34.63	(0.004)		34.65	(0.004)	
37.02	—		37.02	—	
38.94	—		38.94	—	
40.27	—		40.27	—	

^A The ADC(4) calculation according to the proposed model.
^B Complete fourth order calculation.

The results of the ADC(4) and the POLCI calculation are given in Table 6. In the POLCI calculation three new states of $^2\Sigma_g^+$ symmetry arise in the energy range 34–37 eV, which are dominated by 3h–2p configurations and which are not obtained in the SECI calculation. Similarly for $^2\Sigma_u^+$ a state at 32.88 eV and for $^2\Pi_u$ a state at 32.77 eV arises. Furthermore the lowest satellite lines are decreased in energy whilst the corresponding intensities are heavily changed upon the inclusion of double excitations. Another feature of the POLCI results is that the two intense states around 37.5 eV obtained in the SECI calculation merge into a single state. The calculations of Herman *et al.* (1981) using the equation of motion method led to very similar features except that in the higher energy region two intense states were found. In these

Table 6. The ADC(4) and POLCI ionisation energies (eV) for N₂ in an extended basis setPole strengths (in parentheses). They refer to contributions from the $2\sigma_g$ and $3\sigma_g$ orbitals

ADC(4) ^A			POLCI ^B		
	$2\sigma_g$	$3\sigma_g$		$2\sigma_g$	$3\sigma_g$
15.55	—	(0.894)	14.59	—	(0.836)
28.41	(0.084)	(0.016)	28.51	(0.088)	(0.026)
29.41	—	—	34.35	(0.078)	—
30.22	—	—	36.03	(0.054)	(0.014)
34.63	(0.071)	(0.006)	36.96	(0.001)	—
35.79	(0.008)	(0.005)	38.38	(0.528)	(0.001)
35.99	—	—	38.57	(0.014)	—
36.04	(0.001)	—	40.16	(0.005)	—
36.86	(0.001)	(0.002)			
36.95	—	—			
37.78	(0.182)	(0.010)			
38.68	(0.494)	—			
38.97	—	—			
39.92	(0.004)	—			
40.89	—	—			
$1\pi_u$					
16.80	(0.914)		16.49	(0.892)	
28.17	—		32.77	(0.007)	
31.94	(0.006)		39.68	(0.002)	
34.80	—				
35.21	—				
35.23	—				
36.79	—				
37.96	—				
38.06	—				
38.96	(0.003)				
$2\sigma_u$					
18.68	(0.797)		17.60	(0.763)	
24.91	(0.075)		24.27	(0.066)	
25.61	—		—		
25.77	—		—		
33.19	(0.04)		32.88	(0.035)	
35.22	—		—		
38.41	—		37.59	(0.009)	
38.72	—		—		
38.79	—		—		
38.12	(0.002)		—		
39.57	—		—		
39.84	—		41.28	(0.003)	

^A The ADC(4) calculation according to the proposed model with 33 virtual orbitals included in the calculation of the third order terms and 11 in the fourth order terms.^B Results from Langhoff *et al.* (1981).

calculations a number of 3h-2p configurations were included. We expect that the ADC(4) calculations give similar spectral features as the POLCI calculation. This is in general found to be the case as can be seen from Table 6. The additional states (for $^2\Sigma_g$ symmetry three states between 34 and 37 eV, for $^2\Sigma_u$ one at about 33 eV and for $^2\Pi_u$ one at about 32 eV) are found in the ADC(4) calculation as well. They were not obtained in the ADC(3) calculation. Moreover, the lowest satellite lines are now in better agreement with the POLCI results. In the region above 37.5 eV, on the other hand, the ADC(4) calculation gives two peaks. Evidently, this area of the spectrum is strongly dependent on the details of the calculation. Nevertheless, the general trend is still in good qualitative agreement with the CI results. If one analyses the eigenvector components, however, a difference is found. In the POLCI calculation a number of solutions were of predominant 3h-2p character, but in the ADC(4) calculation we do not find solutions of such a type, although we clearly note the qualitative and quantitative effects of the 3h-2p configurations. In an ADC(4) calculation with the double-zeta basis set the situation is again very similar to the one found in the POLCI calculation. The explanation is probably to be found in the fact that in the POLCI calculation the $1\pi_g$ orbital resulting from an SCF calculation on the $(3\sigma_g \rightarrow 1\pi_g)$ $^1\Pi_g$ state was used which is spatially more compact. Only through this expedient was it possible to reveal the relevance of the 3h-2p configurations. In the ADC(4) calculation which employs the $1\pi_g$ orbital from the SCF calculation on the ground state of N_2 the effect of the 3h-2p configurations is probably distributed over many configurations of which none dominates. One further point is that in the ADC(3) calculation the intense $^2\Sigma_u^+$ satellite line of N_2 at about 25 eV is calculated very accurately. This may be surprising. An analysis of the eigenvector for this solution resulting from the ADC(4) calculation reveals that it almost exclusively consists of 2h-1p components. This may in part explain the good agreement found for this satellite line in the ADC(3) calculation.

A comparison of our results with the experimental data of Krummacher *et al.* (1980) is by no means easy. It is quite problematic to identify experimentally all lines in the spectrum of N_2 above 25 eV. Some part of the structure can probably only be explained by considering vibronic coupling among closely spaced states. The main results of the synchrotron radiation study are the identification of the satellite lines at about 25 and 29 eV, of a broad band between 30 and 35 eV with low intensity and of a complex structure above 37 eV with a prominent peak superimposed (Krummacher *et al.* 1980). This latter band when recorded at higher resolution reveals a complex substructure. The satellite line at about 25 eV arises from $2\sigma_u$ ionisation and the intense satellite line at about 29 eV is assigned as the $^2\Sigma_g^+$ state calculated at 28.41 eV in the ADC(4) calculation and at 28.51 eV in the POLCI calculation. This line borrows intensity both from $2\sigma_g$ and from $3\sigma_g$ ionisation. The low intensity band between 30 and 35 eV was in the work of Langhoff *et al.* (1981) assigned essentially to the $^2\Sigma_g^+$, $^2\Sigma_u^+$ and $^2\Pi_u$ states in the energy range between 32 and 35 eV which are of predominant 3h-2p character. The ADC(4) calculation agrees with this assignment. The relatively intense band above 37 eV arises from the single intense state at 38.38 eV according to the POLCI calculation and from the states at 37.78 and 38.68 eV according to the ADC(4) calculation. All these states arise from $2\sigma_g$ ionisation. A detailed understanding of the features of this band probably has to deal with vibronic coupling among closely spaced states of the same symmetry as mentioned above (see also Schirmer *et al.* 1977; Langhoff *et al.* 1981).

7. Low Energy Satellite Lines of CS₂

In the photoelectron spectrum of the CS₂ molecule as recorded by Turner (1970) and Åsbrink and coworkers (Schirmer *et al.* 1979) or Reineck *et al.* (1984) one observes below 20 eV four ionic main states and, in addition, two satellite lines at 14.1 and 17.1 eV. At higher energy (i.e. above 20 eV) one expects the bands corresponding to the inner valence $5\sigma_g$ and $4\sigma_u$ orbitals. Instead a broad band with unusual structure is observed (for details see Allan *et al.* 1972; Carnovale *et al.* 1981). This part of the spectrum clearly exhibits the breakdown of the orbital model of ionisation (Schirmer *et al.* 1979); this fact was shown by a 2ph-TDA calculation. We do not consider this energy range here but instead concentrate on the lowest energy satellite lines of $^2\Pi_u$ symmetry.

Table 7. Lowest ionisation energies (eV) of CS₂ arising from electron ejection out of the $2\pi_u$ orbital

Pole strengths are in parentheses				
ADC(3)	ADC(4) ^A	ADC(4) ^B	ADC(4) ^C	Exp. ^D
12.63 (0.53)	12.43 (0.70)	12.53 (0.73)	12.62 (0.67)	12.9
13.73 (0.20)	14.32 (0.035)	14.61 (0.026)	14.36 (0.047)	14.1
13.88 —	14.79 —	15.08 —	14.79 —	
14.60 (0.004)	15.50 (0.004)	15.88 (0.005)	15.51 (0.005)	
18.04 (0.14)	17.61 (0.16)	17.88 (0.14)	17.67 (0.17)	17.1

^A Fourth order calculation according to the proposed simplified model. The lowest 11 virtual orbitals were used in the calculation of the fourth order terms and the lowest 29 virtual orbitals in the third order terms.

^B As in note A but with 17 virtual orbitals in the fourth order terms.

^C Complete fourth order calculation with 11 virtual orbitals included in the calculation of the fourth order terms and 29 in the third order terms.

^D Schirmer *et al.* (1979).

A SCF calculation employing the [11s7p1d]/(5s4p1d) basis set of Salez and Veillard (1968) for the C atom and the [12s9p2d]/(7s5p2d) basis of Veillard (1968) for the S atom was performed. The ADC(3) calculation reported here nearly exhausted this basis set, but in the ADC(4) calculation according to the model proposed here only a few orbitals were included in the first calculations. Hence the results reported here (Table 7) are preliminary. In the ADC(3) calculation, in general, good agreement with experiment is obtained for the main ionic states except for $^2\Pi_u$ symmetry where the intensity distribution is unacceptable. One obtains two satellite lines of strong intensity. The first one has an intensity of about 40% of the intensity of the main line and it is separated from the latter by about 1 eV. In the experiment, on the other hand, the intensity ratio between the main and satellite line is about 10. The other satellite line appears at higher energy and its intensity is lower than the first one in contrast to experiment. The description given by the ADC(3) method is clearly insufficient. The wrong intensity distributions of the first two lines arise from a separation which is too close. In the ADC(4) calculation, the difficulties disappear (see Table 7). The main line is decreased in energy, and the intensity is increased by about 40%. Moreover, the first satellite line loses most of its intensity while the energy remains essentially unchanged. For the second satellite line we obtain a slight decrease in the intensity and an appreciable energy lowering. These results indicate the relevance of the fourth

order terms. Altogether we obtain an important improvement in the satellite lines when compared with experiment. The energies are quite satisfactory and the intensity distribution is in accord with experiment. More extended calculations involving more orbitals are in progress.

8. Summary

The ADC(3) method discussed in this article is of very wide applicability. If the pole search algorithm is used to solve the equations one can obtain all solutions in a preset energy interval, but for larger molecules it is not possible to exhaust the basis sets. If the Davidson diagonalisation method is used, the basis sets can be exhausted but one does not have a systematic means of obtaining all solutions. For N_2 we have shown that the two numerical tools give results in quite close agreement with each other. For *p*-quinodimethane and for *p*-benzoquinone the Davidson diagonalisation approach is only used to calculate a few ionisation energies. If the OVGF method is applicable, the agreement with these results is very good. In *p*-quinodimethane it was seen that, in agreement with earlier work, the $1b_{2g}$ line splits by many-body effects into two strong components which contribute to the second and third band systems of the PES. For *p*-benzoquinone we confirmed the presently accepted ordering of the first four ionic states which is n_+ , n_- , π_+ , π_- with increasing binding energy. Applications to the ionisation energies of the transition metal diatomics Cu_2 , Ag_2 , Cr_2 and Mo_2 led to results in quite good agreement with the available experimental data, but they also disclosed some problems in the calculations on such systems. A third order perturbation treatment of the ground state appears to be insufficient in some cases, such as for Cr_2 and Mo_2 .

The ADC(3) approach is in general inadequate for describing satellite lines quantitatively. A fourth order description is necessary but computationally very demanding. A simplified ADC(4) approximation was presented and results were discussed for N_2 . It appears from the first calculations that many of the computationally cumbersome terms which arise in fourth order can be omitted. The method thus becomes computationally tractable and still preserves the essential effects of the fourth order terms. An example of the failure of the ADC(3) method in describing satellite lines was found for the CS_2 molecule where the intensity distribution is wrong. Preliminary calculations by the proposed simplified ADC(4) model showed that inclusion of the fourth order terms resolves the problems and leads to quite reasonable agreement with experiment.

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