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To cite this article: J Schirmer and L S Cederbaum 1978 J. Phys. B: Atom. Mol. Phys. 11 1889

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The two-particle-hole Tamm-Dancoff approximation (2ph-TDA) equations for closed-shell atoms and molecules

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Received 13 December 1977

Abstract. An approximation scheme for the one-particle Green's function referred to as the two-particle-hole Tamm-Dancoff approximation (2ph-TDA) is introduced by means of a well defined infinite partial summation of the perturbation expansion for the so-called self-energy part. A spin-free formulation of the working equations is presented for molecular applications. It is demonstrated that the 2ph-TDA is a useful tool for a theoretical treatment of inner valence ionisation processes. A discussion of the physical content and the relationship to other approaches shows the central role of this approximation.

1. Introduction

The usefulness of one-particle Green's functions and related many-body methods for calculating electron ionisation and attachment spectra has been amply demonstrated by many authors. For an account and references the reader is referred to a recent review article by Cederbaum and Domcke (1977). In particular, accurate ionisation potentials, electron affinities and spectral strengths have been obtained for the energy region of outer valence electrons of atoms and molecules by Cederbaum *et al* (1975) and von Niessen *et al* (1977). These accurate calculations result from an approximation scheme for the Green's function specially devised for the valence region (Cederbaum 1973, 1975a). This method makes use of the fact that the ionisation and attachment process is well described by the creation of a quasi-hole and a quasi-particle, respectively. In contrast to the outer valence region, the interesting inner valence region has not as yet proved to be accessible even qualitatively. Here, the quasi-particle picture is no longer valid and, correspondingly, new classes of approximation become essential in order to describe the phenomena which occur.

Approximation schemes which are adequate beyond the quasi-particle picture have been proposed and investigated by several authors. Pickup and Goscinski (1973) and Purvis and Öhrn (1974) have used the super-operator formalism of Goscinski and Lukman (1970) to obtain decoupled equations for the one-particle Green's function. An alternative approach via the equations-of-motion formalism of Rowe (1968) was first proposed by Simons and Smith (1973) and later completed by Purvis and Öhrn (1975) and Jørgensen and Simons (1975). Approximations for the so-called self-energy part Σ , related to the Green's function via the Dyson equation, have been derived by means of infinite partial summations of the perturbation expansion of Σ (Cederbaum 1974, 1975b, Schirmer 1977). A thorough discussion of the latter methods is given by

0022-3700/78/0011-1889 \$02.00 © 1978 The Institute of Physics

Cederbaum and Domcke (1977). It should be noted that related work in the field of nuclear physics has been reported by Schuck *et al* (1973) and by Ring and Schuck (1974).

In spite of the theoretical effort, only a few many-body calculations for the inner valence and core region have been carried out (see, for example, Cederbaum 1974, Purvis and Öhrn 1974). Furthermore, these calculations remain considerably behind the theoretical achievements since crude additional approximations are introduced in order to meet the severe computational difficulties arising from the large dimension of the resulting system of equations. It is the aim of this work to describe an approximation scheme called the two-particle-hole Tamm-Dancoff approximation (2ph-TDA) and to demonstrate that this method provides us with useful information for the whole energy scale. Although this method or closely related approximations emerge from a variety of approaches already quoted, no rigorous application has hitherto been carried out. The numerical evidence arising from the calculations for a number of molecules shows that the outer valence ionisation energies are fairly well reproduced, i.e. better than by Koopmans' theorem (Koopmans 1933). The most important point, however, is the qualitatively correct description of the inner valence region, where some striking features are revealed. It is found that in general complete break-down of the molecular-orbital picture occurs. Instead of one line arising due to the ionisation of an electron in a given shell, there often appear two or more lines with comparable strengths so that it is no longer possible to discern main and satellite lines (Cederbaum et al 1977, Schirmer et al 1977).

The present work is divided into two parts. In this paper we shall establish the theoretical foundations of the 2ph–TDA method. In the following paper we report on its numerical application to three diatomic molecules containing a second-row atom.

In §2 of this paper the 2ph–TDA equations are introduced by means of a well defined infinite partial summation of Feynman diagrams in the perturbation expansion of the self-energy part Σ . A spin-free formulation of the 2ph–TDA equations representing the starting point for molecular calculations is presented in §3. In §4 we investigate the 2ph–TDA from a wavefunction point of view in order to provide some further physical insight into this approximation. A discussion of the 2ph–TDA in comparison with these approaches (in particular, with the work of Simons and Smith (1973), Pickup and Goscinski (1973) and Parvis and Öhrn (1974)) will conclude this article.

2. Derivation of the 2ph-TDA equations

We start from the Hamiltonian

$$H = \sum \epsilon_i c_i^{\dagger} c_i + \frac{1}{2} \sum V_{ijkl} c_i^{\dagger} c_j^{\dagger} c_l c_k + \sum v_{ij} c_i^{\dagger} c_j$$
(1)

of an electronic system in second quantised notation. Here c_i (c_i^{\dagger}) is a destruction (creation) operator for a one-particle state $|\varphi_i\rangle$ of a suitably chosen one-particle basis. The other quantities are the one-particle energies ϵ_i , the Coulomb matrix elements

$$V_{ijkl} = \int d\mathbf{r}_1 d\mathbf{r}_2 \, \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \, V(\mathbf{r}_1 - \mathbf{r}_2) \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2)$$

and additional one-particle matrix elements v_{ii} . In the case of a Hartree-Fock basis

the latter quantities are given by

$$v_{ij} = -\sum_{k} V_{ik[jk]} n_k$$

$$V_{ij[kl]} = V_{ijkl} - V_{ijlk}.$$
(2)

The summation runs over occupied states only, due to the occupation numbers $n_k = 1, 0$ for occupied and unoccupied states, respectively, with respect to the Hartree-Fock ground state $|\phi_0\rangle$. It is also useful to introduce the quantity $\bar{n}_k = 1 - n_k$.

The one-particle Green's function **G** is defined by (Thouless 1961)

$$G_{pq}(t,t') = -i\langle \Psi_0 | Tc_p(t) c_q^{\dagger}(t) | \Psi_0 \rangle$$
(3a)

where $|\Psi_0\rangle$ is the exact ground state, T is Wick's time-ordering operator and $c_q(t) = e^{iHt} c_q e^{-iHt}$ denotes the destruction operator in the Heisenberg picture. The Fourier-transformed Green's function is easily obtained from equation (3a) and reads

$$G_{pq}(\omega) = \sum_{m} \frac{x_{p}^{(m)} x_{q}^{(m)*}}{\omega + E_{0}^{(N)} - E_{m}^{(N+1)} + i\eta} + \sum_{n} \frac{x_{p}^{(n)} x_{q}^{(n)*}}{\omega + E_{n}^{(N-1)} - E_{0}^{(N)} - i\eta}$$

$$x_{p}^{(m)} = \langle \Psi_{0} | c_{p} | \Psi_{m}^{(N+1)} \rangle \qquad x_{p}^{(n)} = \langle \Psi_{n}^{(N-1)} | c_{p} | \Psi_{0} \rangle$$
(3b)

where η denotes a positive infinitesimal. $|\Psi_i^{(M)}\rangle$ and $E_i^{(M)}$ are the exact eigenstates and energies of the interacting *M*-fermion system. **G** is related to the so-called self-energy part Σ by the Dyson equation which, in matrix notation in ω space, is given by

$$\mathbf{G}(\omega) = \mathbf{G}^{0}(\omega) + \mathbf{G}^{0}(\omega) \, \boldsymbol{\Sigma}(\omega) \mathbf{G}(\omega). \tag{4}$$

The 'free' Green's function \mathbf{G}^{0} introduced here refers to the diagonal one-particle Hamiltonian and the unperturbed state $|\phi_{0}\rangle$. In the ω representation one obtains

$$G_{pq}^{0} = \delta_{pq} \left(\frac{n_p}{\omega - \epsilon_p - i\eta} + \frac{\bar{n}_p}{\omega - \epsilon_p + i\eta} \right).$$
(5)

As is well known, there exists a perturbation expansion of $\Sigma(\omega)$ in terms of the interaction matrix elements V_{ijkl} and v_{ij} represented by Feynmann (or Abrikosov) diagrams. The rules for constructing and evaluating the corresponding diagrams are discussed extensively in several works (Abrikosov *et al* 1965, Csanak *et al* 1971).

For our purpose we recall the contributions up to second order. In first order (given diagrammatically in figure 1(a)) we have a constant (ω -independent) contribution

$$\Sigma_{pq}^{(1)} = v_{pq} + \sum_{k} V_{pk[qk]} n_k \tag{6}$$

which vanishes for the case of a Hartree–Fock basis as can be seen from equation (2). Corresponding to the two (time-ordered) diagrams in figure 1(b), the second-order contribution

$$\Sigma_{pq}^{(2)}(\omega) = \frac{1}{2} \sum \frac{V_{pj[kl]} V_{qj[kl]}}{\omega + \epsilon_j - \epsilon_k - \epsilon_l - i\eta} \bar{n}_j n_k n_l + \frac{1}{2} \sum \frac{V_{pj[kl]} V_{qj[kl]}}{\omega + \epsilon_j - \epsilon_k - \epsilon_l + i\eta} n_j \bar{n}_k \bar{n}_l \tag{7}$$

is composed of two parts, the sums of simple poles in the upper and lower complex planes, respectively.

It is interesting to note that the exact self-energy part possesses the same analytical structure as that exhibited by the second-order expression (7). As can be shown from



Figure 1. Goldstone diagrams for the self-energy part in Abrikosov notation. (a) First-order contribution. The \times vertex represents the one-particle interaction matrix elements v_{ij} . (b) The diagrams of second order. (c) The 2h1p diagrams up to fourth order. The 2p1h diagrams are obtained by drawing the diagrams upside down.

the spectral resolution of **G** and the Dyson equation, $\Sigma(\omega)$ can be written as a sum (Cederbaum 1975b)

$$\Sigma(\omega) = \Sigma(\infty) + \mathbf{M}(\omega) \tag{8}$$

of a constant part $\Sigma(\infty)$ and an ω -dependent part $\mathbf{M}(\omega)$ which is the sum of simple poles. In analogy to the second-order contribution we write $\mathbf{M}(\omega)$ as a sum

$$\mathbf{M}(\omega) = \mathbf{M}^{(I)}(\omega) + \mathbf{M}^{(II)}(\omega)$$

where $\mathbf{M}^{(l)}(\mathbf{M}^{(li)})$ is analytic in the lower (upper) complex plane.

By expanding the self-energy part up to second order one clearly obtains an approximation going beyond the one-particle (Hartree-Fock) level. As is suggested by the poles of $\mathbf{M}^{(2)}(\omega)$, new processes occur which are associated with the removal (addition) of an electron accompanied by a particle-hole excitation. In the following the two kinds of process will be referred to as two-hole-one-particle (2h1p) excitations and two-particle-one-hole (2p1h) excitations, respectively. Diagrammatically, the 2h1p excitations are associated with two hole lines (lines pointing downwards) and one particle line (line pointing upwards) connecting two subsequent interaction points, this being the case in the first diagram of figure 1(b). There exists a well distinguished class of diagrams (2h1p diagrams) up to infinite order where only 2h1p excitations are present, i.e. where for all diagrams any two subsequent interaction points are connected by two hole lines and one particle line. The 2h1p diagrams up to fourth order are shown in figure 1(c). Analogously, there is a class of 2p1h diagram related to the 2p1h excitations. In this case two subsequent interaction points are connected by two particle lines and one hole line. Due to the simple construction principle both classes of diagram can be summed exactly as will be outlined in the following.

We restrict ourselves for the moment to the 2h1p case (I). It is convenient to separate the two outer interaction points by introducing the so-called kernel $\Gamma^{(I)}$:

$$M_{pq}^{(l)}(\omega) = \frac{1}{4} \sum_{(l)} V_{pj[kl]} \Gamma_{jkl,j'k'l'}^{(l)}(\omega) V_{qj'[k'l']}.$$
(9)

The matrix $\Gamma^{(1)} \equiv (\Gamma^{(1)}_{jkl,j'k'l'})$ is restricted to the sets of indices (j, k, l) and (j', k', l') with $\bar{n}_j n_k n_l = \bar{n}_{j'} n_{k'} n_{l'} = 1$. $\Gamma^{(1)}$ is chosen to be antisymmetric with respect to the indices k, l (and k', l'). Now the construction principle for the 2h1p diagrams can easily be converted



Figure 2. Graphical representation of the summation of 2h1p diagrams.

into a recursion relation for $\Gamma^{(1)}$. Its graphical representation is given in figure 2. The corresponding equation reads

$$\Gamma^{(1)} = (\omega \mathbf{1} - \mathbf{K}^{(1)})^{-1} \gamma^{0} + (\omega \mathbf{1} - \mathbf{K}^{(1)})^{-1} \tilde{\mathbf{C}}^{(1)} \Gamma^{(1)}$$
(10a)

with

$$K_{jkl,j'k'l'}^{(l)} = (-\epsilon_j + \epsilon_k + \epsilon_l)\delta_{jj'}\delta_{kk'}\delta_{ll'}$$
(10b)

$$\tilde{C}_{jkl,j'k'l'}^{(l)} = \frac{1}{2} V_{kl[k'l']} \delta_{jj'} - \delta_{ll'} V_{jl'[j'l]} - \delta_{kk'} V_{jk'[j'k]}$$

$$\bar{n}_i n_k n_l = \bar{n}_{i'} n_{k'} n_{l'} = 1.$$
(10c)

The matrix
$$\gamma^0$$
 is a unit matrix antisymmetrised with respect to k, $l(k'l')$,

$$\gamma_{jkl,j'k'l'}^{0} = \delta_{jj'} (\delta_{kk'} \delta_{ll'} - \delta_{kl'} \delta_{lk'}) \tag{11}$$

guaranteeing the correct symmetry (with respect to index exchange) of $\Gamma^{(l)}$. The formal solution of equation (10*a*) is given by

$$\boldsymbol{\Gamma}^{(1)} = (\omega \mathbf{1} - \mathbf{K}^{(1)} - \tilde{\mathbf{C}}^{(1)})^{-1} \boldsymbol{\gamma}^{0}.$$
(12)

An analogous treatment applies for the 2p1h case (II). Here the sets of indices (j, k, l) and (j', k', l') are restricted by $n_i \bar{n}_k \bar{n}_l = 1$. The corresponding equations are

$$M_{pq}^{(II)} = \frac{1}{4} \sum_{(II)} V_{pj[kl]} \Gamma_{jkl,j'k'l'}^{(II)}(\omega) V_{qj'[k'l']}$$
(13)

$$\Gamma^{(\mathrm{II})} = (\omega \mathbf{1} - \mathbf{K}^{(\mathrm{II})} - \tilde{\mathbf{C}}^{(\mathrm{II})})^{-1} \gamma^{0}$$
(14a)

with

$$K_{jkl,j'k'l'}^{(1)} = (-\epsilon_j + \epsilon_k + \epsilon_l)\delta_{jj'}\delta_{kk'}\delta_{ll'}$$
(14b)

$$\tilde{C}_{jkl,j'k'l'}^{(ll)} = -\frac{1}{2}\delta_{jj'}V_{kl[k'l']} + \delta_{ll'}V_{jl'[j'l]} + \delta_{kk'}V_{jk'[j'k]}$$
(14c)

$$n_{j}\bar{n}_{k}\bar{n}_{l} = n_{j'}\bar{n}_{k'}\bar{n}_{l'} = 1.$$

It should be noted that for the case of non-vanishing first-order contributions $\Sigma_{ij}^{(1)} \neq 0$, the constant matrices $\tilde{\mathbf{C}}^{(1)} (\tilde{\mathbf{C}}^{(II)})$ have to be supplemented by an additional matrix $\tilde{\mathbf{S}}^{(l)} (\tilde{\mathbf{S}}^{(II)})$ given by

$$S_{jkl,j'k'l'}^{(I,II)} = -\delta_{kk'}\delta_{ll'}s_{jj'} + \delta_{jj'}\delta_{kk'}s_{ll'} + \delta_{jj'}\delta_{ll'}s_{kk'}$$
(15a)

with $\bar{n}_j n_k n_l = \bar{n}_{j'} n_{k'} n_{l'} = 1$ for case (I) and $n_j \bar{n}_k n_l = n_{j'} \bar{n}_{k'} \bar{n}_{l'} = 1$ for case (II), where

$$s_{ij} = \Sigma_{ij}^{(1)}.$$
 (15b)

Due to the close analogy of the infinite partial summations in (12) and (14) with the Tamm-Dancoff approximation (TDA) for the particle-hole propagator (see, for instance, Lane 1964) the approximation described above for $\mathbf{M}(\omega)$ will be referred to as 2ph-TDA.

The remaining task is to determine the corresponding constant part $\Sigma(\infty)$. The exact constant part satisfies the relation (Cederbaum and Domcke 1977)

$$\Sigma_{pq}(\infty) = v_{pq} + \sum_{kk'} V_{pk[qk']} \frac{1}{2\pi i} \oint G_{k'k}(\omega) \,\mathrm{d}\omega \tag{16}$$

which follows from the diagram of figure 1(a) by inserting the full G line instead of the free G^0 line. The contour integral has to be closed in the upper complex plane.

Expressing **G** by the solution of the Dyson equation

$$\mathbf{G} = [(\mathbf{G}^{0})^{-1} - \mathbf{\Sigma}(\infty) - \mathbf{M}(\omega)]^{-1}$$
(17)

one obtains an implicit equation for $\Sigma(\infty)$, once $\mathbf{M}(\omega)$ or an approximation to it is given.

The final 2ph-TDA result for the self-energy is thus given by

$$\Sigma(\omega) = \Sigma(\infty) + \mathbf{M}^{(I)}(\omega) + \mathbf{M}^{(II)}(\omega)$$
(18)

where $\mathbf{M}^{(1)}$ and $\mathbf{M}^{(11)}$ are the 2h1p and 2p1h summations described above and $\Sigma(\infty)$ follows from equations (16) and (17) with $\mathbf{M}(\omega) = \mathbf{M}^{(1)}(\omega) + \mathbf{M}^{(11)}(\omega)$. The Green's function obtained by solving the Dyson equation (4) with the 2ph–TDA self-energy part of equation (18) will be referred to as the 2ph–TDA Green's function.

3. Spin-free formulation of the working equations

For numerical calculations it is important to reduce the space of the 2h1p and 2p1h problems (given by equations (12) and (14), respectively) by making use of the inherent symmetry properties. For molecular calculations, in particular, it is essential to obtain a formulation of the equations in terms of spin-free orbitals. Such a symmetry reduction is presented in the following. Since the procedure applies to both 2h1p and 2p1h problems, we simplify the notation by omitting the superscripts (I) and (II) whenever unessential.

As a first step the index space (jkl) will be restricted to k < l. One simply makes use of the antisymmetry property of Γ with respect to exchange of k and l (k' and l') and the related properties of $\tilde{\mathbf{C}}$ and γ^0 . The resulting equations are

$$M_{pq}(\omega) = \sum_{\substack{j,k(19)$$

$$\boldsymbol{\Gamma}(\boldsymbol{\omega}) = (\boldsymbol{\omega}\mathbf{1} - \mathbf{K} - \mathbf{C})^{-1}.$$
(20)

Here

$$C_{jkl,j'k'l'} = \bar{C}_{jkl,j'k'l'} - \bar{C}_{jkl,j'l'k'}$$
(21)

is antisymmetrised with respect to k, l(k', l') and all quantities are reduced to k < l(k' < l').

It is convenient to reformulate the inversion problem of equation (20) as a matrix diagonalisation. Let $\omega^{(n)}$ and $x_{jkl}^{(n)}$ denote the *n*th eigenvalues and the amplitudes of the corresponding eigenvector, respectively, for the following eigenvalue problem:

$$(\omega^{(n)} + \epsilon_j - \epsilon_k - \epsilon_l) x_{jkl}^{(n)} - \sum_{j',k' < l'} C_{jkl,j'k'l'} x_{j'k'l'}^{(n)} = 0.$$

$$(22)$$

Then Γ is given by

$$\Gamma_{jkl,j'k'l'} = \sum_{n} \frac{x_{jkl}^{(n)} x_{j'k'l'}^{(n)*}}{\omega - \omega^{(n)}}$$
(23)

and the corresponding self-energy part reads

$$M_{pq}(\omega) = \sum_{n} \frac{m_p^{(n)} m_q^{(n)*}}{\omega - \omega^{(n)}}$$
(24)

with the amplitudes

$$m_p^{(n)} = \sum_{j,k
(25)$$

As will become clear from §4 the amplitudes $x_{jkl}^{(n)}$ can be regarded as the coefficients of the term $c_j^{\dagger}c_k c_l |\phi_0\rangle$ in an expansion of an (N-1)-particle state $(c_j c_k^{\dagger} c_l^{\dagger} |\phi_0\rangle$ in an analogous expansion of an (N + 1)-particle state). In order to get symmetry reductions one has to construct linear combinations of the amplitudes such that they correspond to eigenstates of the symmetry operators of the system, in particular of the spin operators \hat{S}^2 and \hat{S}_z . These symmetry-adapted amplitudes are denoted by $x_{ikl}^{(s,Ms)}$.

In what follows we split the spin-orbital indices into a spin-free orbital index denoted by an italic letter and a spin index denoted by a greek letter, namely $j \rightarrow j\gamma$. As is the common notation, α and β stand for spin projection $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$, respectively. For the orbital indices j, k, l there occur eight amplitudes $x_{j\gamma k\chi l\lambda}$. Let us first consider the amplitudes with the spin indices $\beta\alpha\alpha$:

$$x_{ikl}^{(3/2, -3/2)} = x_{i\beta k\alpha l\alpha} \qquad k < l.$$
⁽²⁶⁾

In accordance with the fact that $c_{j\beta}^{\dagger}c_{k\alpha}c_{l\alpha}|\phi_0\rangle$ is an eigenstate of \hat{S} and \hat{S}_z with $S = \frac{3}{2}$ and $M_S = -\frac{3}{2}$, one obtains a decoupled equation for these amplitudes. However, since no quartet state can arise from a one-particle transition of a closed-shell ground state, there result no contributions to the self-energy part. This can be seen explicitly by noticing that the matrix elements by which the amplitudes of equation (26) are multiplied according to equation (25) vanish:

$$V_{p_{\gamma}j\beta[kala]} = 0. \tag{27}$$

Therefore, one can leave out the decoupled block of the eigenvalue equation for the quartet amplitudes.

Next we look at the three amplitudes $x_{j\alpha k\alpha l\alpha}$, $x_{j\beta k\alpha l\beta}$ and $x_{j\beta k\beta l\alpha}$ corresponding to $M_S = -\frac{1}{2}$ (for k = l only $x_{j\beta k\alpha k\beta}$ has to be considered). Due to the coupling rules of three particles with spin $\frac{1}{2}$ there are two independent states with $S = \frac{1}{2}$ and the $M_S = -\frac{1}{2}$ component of the quartet state. Associated with the latter state are the amplitudes

$$x_{jkl}^{(3/2, -1/2)} = (1/\sqrt{3}) \left(-x_{j\alpha k\alpha l\alpha} + x_{j\beta k\alpha l\beta} + x_{j\beta k\beta l\alpha} \right) \qquad k < l.$$
(28)

The decoupled equations for these amplitudes are identical to those of the amplitudes (26), and again no contribution for the self-energy part arises because of the identity

$$-V_{p\gamma j\alpha[k\alpha l\alpha]} + V_{p\gamma j\beta[k\alpha l\beta]} + V_{p\gamma j\beta[k\beta l\alpha]} = 0.$$
⁽²⁹⁾

The two remaining independent linear combinations corresponding to the two $S = \frac{1}{2}$ states are not determined uniquely. There exists, however, a distinct choice leading to antisymmetric amplitudes $x_{jkl}^{(1/2, -1/2)}$ and symmetric amplitudes $x_{jkl}^{(1/2, -1/2)}$ with respect to exchange of the spatial indices k and l:

$$d_{jkl} \equiv x_{jkl}^{(1/2, -1/2)} = (1/\sqrt{2}) (x_{j\beta k\alpha l\beta} - x_{j\beta k\beta l\alpha}) \qquad k < l$$

$$f_{jkl} \equiv x_{jkl}^{\prime(1/2, -1/2)} = \begin{cases} (1/\sqrt{6}) \left(2x_{j\alpha k\alpha l\alpha} + \dot{x}_{j\beta k\alpha l\beta} + x_{j\beta k\beta l\alpha}\right) & k < l \quad (30) \\ x_{j\beta k\alpha k\beta} & k = l. \end{cases}$$

The remaining amplitudes correspond to $M_s = \frac{1}{2}$ and $M_s = \frac{3}{2}$ and provide no new

equations. Thus we have reduced the eight spin-dependent amplitudes $x_{j\gamma k\chi l\lambda}$ for a given triplet of spatial indices to the two (spin-independent) amplitudes of equation (30). In matrix notation the resulting equations for these amplitudes are given as follows:

$$\begin{pmatrix} \omega \mathbf{1} - \mathbf{K} - \mathbf{F} & -\mathbf{H} \\ -\mathbf{H}^{\dagger} & \omega \mathbf{1}' - \mathbf{K}' - \mathbf{D} \end{pmatrix} \begin{pmatrix} f \\ d \end{pmatrix} = \mathbf{0}.$$
 (31)

Here (the prime on **K** and **1** indicates that the index space is restricted to $k \neq l$)

$$\begin{split} F_{jkl,j'k'l'} &= F_{jkl,j'k'l'} + F_{jkl,j'l'k'} & k < l, k' < l' \\ F_{jkk,j'k'l'} &= \sqrt{2} \, \tilde{F}_{jkk,j'k'l'} & k' < l' \\ F_{jkl,j'kk'} &= \sqrt{2} \, \tilde{F}_{jkl,j'k'k'} & k < l \\ F_{jkk,j'k'k'} &= \tilde{F}_{jkk,j'k'k'} \\ H_{jkl,j'k'l'} &= \tilde{H}_{jkl,j'k'l'} - \tilde{H}_{jkl,j'l'k'} & k < l, k' < l' \\ H_{jkk,j'k'l'} &= \sqrt{2} \, \tilde{H}_{jkk,j'k'l'} & k' < l' \\ \end{bmatrix}$$

with

$$\vec{F}_{jkl,j'k'l'} = \mp \left[\delta_{jj'} \frac{1}{2} (V_{klk'l'} + V_{kll'k'}) - \delta_{kk'} (V_{jl'j'l} - \frac{1}{2} V_{jl'lj'}) - \delta_{ll'} (V_{jk'j'k} - \frac{1}{2} V_{jk'kj'}) \right] \\ \vec{D}_{jkl,j'k'l'} = \mp \left[\delta_{jj'} \frac{1}{2} V_{kl[k'l']} - \delta_{kk'} (V_{jl'j'l} - \frac{3}{2} V_{jl'lj'}) - \delta_{ll'} (V_{jk'j'k} - \frac{3}{2} V_{jk'kj'}) \right]$$
(32)

$$\widetilde{H}_{jkl,j'k'l'} = \mp \sqrt{\frac{3}{2}} (\delta_{kk'} V_{jl'lj'} - \delta_{ll'} V_{jk'kj'}).$$

In these expressions for \tilde{F} , \tilde{D} and \tilde{H} the upper sign applies for the 2h1p case and the lower sign for the 2p1h case.

Having solved the secular equation (31), the self-energy part is easily obtained via

$$M_{pq}(\omega) = \sum_{n} \frac{m_{p}^{(n)} m_{q}^{(n)*}}{\omega - \omega^{(n)}}$$
(33)

with

$$m_{p}^{(n)} = \frac{1}{\sqrt{2}} \sum_{j,k(34)$$

Equations (31)–(34) constitute the spin-free formulation of the 2h1p–TDA and 2p1h–TDA for the self-energy part. In a similar way one can make use of the spatial symmetry to achieve further reductions. In the case of atoms one has to consider the angular momentum coupling schemes for three particles. For molecules one has to construct the irreducible representations out of the three-fold products of the symmetry orbitals. This analysis is particularly simple for the case of a symmetry group (or a subgroup) possessing only one-dimensional representations. Here each amplitude corresponds to an irreducible representation and amplitudes with different irreducible representations decouple.

4. Physical interpretation of the 2ph-TDA equations and discussion

For a further understanding of the 2ph–TDA method an interpretation in terms of wavefunctions seems useful. Expanding the (N - 1)-particle wavefunction in terms of 2h1p excitations on the unperturbed (Hartree–Fock) ground state

$$|\Psi_{\nu}\rangle_{l}^{N-1} = \sum_{\substack{j,k(35)$$

and considering the expansion coefficients as variational parameters, one obtains a secular equation which is identical to equation (22), where the constant matrix **C** is the matrix **C**⁽¹⁾ of equations (21) and (10c) and the excitation energies are $\omega^{(n)} = E_n^{(N-1)} - E_0$, E_0 denoting the (Hartree–Fock) energy corresponding to $|\Phi_0\rangle$. An analogous result is obtained for the expansion

$$|\Psi_{v}\rangle^{N+1} = \sum_{\substack{j,k < l \\ n_{j}n_{k}n_{l}=1}} x_{jkl}^{(v)} c_{j} c_{k}^{\dagger} c_{l}^{\dagger} |\Phi_{0}\rangle$$
(36)

of the (N + 1)-particle state in terms of 2p1h excitations.

The energies and wavefunctions resulting from the expansions (35) and (36), respectively, are unphysical in the sense that the coupling to the one-hole and one-particle excitations have been left unconsidered. Instead of equations (35) and (36) one should deal with the following expansions:

$$|\Psi_{v}\rangle^{N-1} = \sum_{n_{k}=1} x_{k}^{(v)} c_{k} |\Phi_{0}\rangle + \sum_{\substack{j,k < l \\ \overline{n}_{j}n_{k}n_{l}=1}} x_{jkl}^{(v)} c_{j}^{\dagger} c_{k} c_{l} |\Phi_{0}\rangle$$
(37)

$$|\Psi_{v}\rangle^{N+1} = \sum_{\vec{n}_{k}=1} x_{k}^{(v)} c_{k}^{\dagger} |\Phi_{0}\rangle + \sum_{\substack{j,k < l \\ n_{j}\vec{n}_{k}, n_{l}=1}} x_{jkl}^{(v)} c_{j} c_{k}^{\dagger} c_{l}^{\dagger} |\Phi_{0}\rangle.$$
(38)

Let us consider the 2h1p case given by equation (37). The variation of the 1h parameters $x_{(h)}$ and the 2h1p parameters $x_{(phh)}$ leads to a secular equation which, in matrix notation, reads

$$\begin{pmatrix} \omega \mathbf{1} - \boldsymbol{\epsilon} & -\mathbf{V} \\ -\mathbf{V}^{\dagger} & \omega \mathbf{1}^{(1)} - \mathbf{K}^{(1)} - \mathbf{C}^{(1)} \end{pmatrix} \begin{pmatrix} \mathbf{x}_{(h)} \\ \mathbf{x}_{(phh)} \end{pmatrix} = 0.$$
(39)

Here the submatrix $\mathbf{A}_{11} = \omega \mathbf{1} - \boldsymbol{\epsilon}$ corresponds to the occupied orbitals $(n_k = 1), \boldsymbol{\epsilon}$ denoting the diagonal matrix of one-particle energies. The submatrix $\mathbf{A}_{22} = \omega \mathbf{1}^{(1)} - \mathbf{K}^{(1)} - \mathbf{C}^{(1)}$ corresponding to the 2h1p part has already been considered (see equations (10) and (20)). The coupling between the h and the 2h1p part is due to the coupling matrix $\mathbf{A}_{12} = -\mathbf{V}$ with elements

$$(\mathbf{V})_{p,jkl} = V_{pj[kl]}.\tag{40}$$

From equation (3b) it is seen that, once the ground-state and ionic-state wavefunctions are given, one can easily obtain the Green's function explicitly. The Green's function which corresponds to equations (37) and (39) is clearly given by

$$G_{pq} = \sum_{n} \frac{x_p^{(n)} x_q^{(n)*}}{\omega - \omega^{(n)}} \qquad n_p n_q = 1.$$
(41)

А.М.Р.(В) 11/11---В

Here $x_p^{(n)}$ are the variational coefficients in equation (37) and $\omega^{(n)} = E_n^{(N-1)} - E_0$, where the ionic energies $E_n^{(N-1)}$ are the eigenvalues of equation (39). By inverting the matrix

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} \\ \mathbf{A}_{21} & \mathbf{A}_{22} \end{pmatrix}$$

it is straightforward to show that

$$\mathbf{G} = (\mathbf{A}^{-1})_{11}. \tag{42}$$

On the other hand, the transformation of equation (39) into a partitioned form leads to

$$(\mathbf{A}^{-1})_{11} = [\omega \mathbf{1} - \boldsymbol{\epsilon} + \mathbf{V}^{\dagger} (\omega \mathbf{1}^{(1)} - \mathbf{K}^{(1)} - \mathbf{C}^{(1)})^{-1} \mathbf{V}]^{-1}.$$
(43)

Clearly, equations (42) and (43) can be identified with the Dyson equation (17), where the self-energy part is given by the 2h1p result of equation (9),

$$\Sigma(\omega) = \mathbf{M}^{(1)}(\omega) \tag{44}$$

as can be seen by inspection of equations (19), (20) and (10).

Thus, equations (42) and (43) constitute an approximation for the one-particle Green's function **G**—referred to as the h-2h1p approximation—that is fully equivalent to a wavefunction description where the ground state is given by the unperturbed (Hartree-Fock) state $|\Phi_0\rangle$ and the (N-1)-particle states are constructed from all h and 2h1p excitations on $|\Phi_0\rangle$. For the sake of completeness, we mention that an analogous approximation (p-2p1h) results for the (N + 1)-particle case.

In this particular form the h-2h1p (p-2p1h) excitations have been regarded by Arita and Horie (1971), Ring and Schuck (1974) and Schuck *et al* (1973) with the objective of calculating $(N \pm 1)$ -particle excited states of nuclei. For the direct calculation of ionisation energies the h-2h1p approximation of equation (43) has obviously the disadvantage that—whereas reorganisation and correlation effects for the ionic states are partly taken into account—the ground-state correlation remains completely out of consideration.

In contrast to the h-2h1p approximation it is an essential property of the 2ph-TDA that both the 2h1p and the 2p1h parts $\mathbf{M}^{(I)}$ and $\mathbf{M}^{(II)}$ are combined within the selfenergy part according to equation (18) and that there is no decoupling into hole or particle states for the Dyson equation (17). The 2ph-TDA does not allow for a simple description by means of a wavefunction picture. Although related to the h-2h1p (p-2p1h) approximation according to the common equations for the self-energy contributions $\mathbf{M}^{(I)}$ ($\mathbf{M}^{(II)}$) the 2ph-TDA obviously goes beyond the h-2h1p approximation at least in that an important amount of ground-state correlation is taken into account. This is drastically confirmed by the numerical results when one compares both approximations.

It should be stressed that the 2ph–TDA only partially accounts for the ground-state correlation effects. As the derivation in §2 has shown, the exact self-energy part $\Sigma(\omega)$ is only incompletely represented by the 2ph–TDA self-energy part for contributions higher than second order. For the third-order self-energy part $\Sigma^{(3)}(\omega)$, in particular, the contributions of the diagrams in figure 3 which have been shown to be mainly associated with ground-state correlation (Cederbaum and Domcke 1977 §III.D) are missing. In order to incorporate ground-state correlation more extensively, an approximation scheme for the self-energy part has been developed (Cederbaum 1975b, Cederbaum and Domcke 1977, Schirmer 1977) that exhibits the following properties: (i) the 2ph–TDA is contained as a special case, (ii) the self-energy part is exact up to third order and—which is very important—(iii) all diagrams 'directly arising' from the



Figure 3. Goldstone diagrams of third order not taken into account by the 2ph-TDA.

third-order diagrams are summed up to infinite order. Due to the high numerical requirements this method has not been applied so far except for small model systems. The implementation of the 2ph–TDA presented here proves to be crucial for every further study.

It is interesting to note that equations related to the 2ph–TDA equations show up within the framework of an approach given by Simons and Smith (1973). These authors start from the excitation operators

$$\Omega_{(\nu)}^{\dagger} = \sum_{\bar{n}_{k}=1} x_{k}^{(\nu)} c_{k}^{\dagger} + \sum_{\substack{k < l \\ n_{j}\bar{n}_{k}\bar{n}_{l}=1}} x_{jkl}^{(\nu)} c_{j} c_{k}^{\dagger} c_{l}^{\dagger} + \sum_{\substack{k < l \\ \bar{n}_{j}n_{k}n_{l}=1}} y_{jkl}^{(\nu)} c_{j} c_{k}^{\dagger} c_{l}^{\dagger}$$
(45)

and a correlated ground-state wavefunction given by

$$|0\rangle = N^{-1/2} \left(1 + \sum_{\substack{k < l \\ m < n}} r_{klmn} c_k^* c_l^* c_m c_n \right) |\Phi_0\rangle \qquad \bar{n}_k \bar{n}_l n_m n_n = 1$$
(46)

where the coefficients r_{klmn} are determined from Rayleigh–Schrödinger perturbation theory. The excitation operator of equation (45) contains—with respect to the 2p1h expansion of equation (38)—additional amplitudes $y_{jkl}^{(v)}$ corresponding to the 2h1p space. By evaluating the equations of motion for the excitation operators $\Omega_{(v)}^+$ working on the wavefunction $|0\rangle$ and retaining only terms up to third order in the electronic interaction one arrives at a self-energy part whose ω -dependent contribution is of the form

$$\mathbf{M}(\omega) = \mathbf{B} \, \Gamma(\omega) \mathbf{B}^{\dagger} = \mathbf{B}^{(\mathrm{I})} \Gamma^{(\mathrm{I})}(\omega) \mathbf{B}^{(\mathrm{I})} + \mathbf{B}^{(\mathrm{II})} \Gamma^{(\mathrm{II})}(\omega) \mathbf{B}^{(\mathrm{II})}. \tag{47}$$

Here $\Gamma^{(I)}(\omega)$ and $\Gamma^{(II)}(\omega)$ are identical to the 2h1p and 2p1h parts, respectively, of the 2ph–TDA self-energy part. It should be noted that in the original paper of Simons and Smith only a diagonal version of the 2ph–TDA equations for $\Gamma^{(I)}(\Gamma^{(II)})$ appears. This deficiency has been recognised by Purvis and Öhrn (1975) who present the correct equations. In actual calculations, however, Simons and co-workers do not make use of the full 2h1p (2p1h) equations for the poles of the self-energy part.

Whereas the poles of the self-energy part within the approach of Simons and Smith are determined by the 2ph–TDA equations, the corresponding residues differ from the 2ph–TDA in that the matrices $\mathbf{B}^{(1,1)}$ contain terms of second order in the electronic interaction. The resulting self-energy part is consistent through third order. Here a remark might be appropriate. The question arises whether it is a good approximation to obtain the poles of the self-energy part from an infinite partial summation (including all orders of the electronic interaction) and on the other hand to calculate the residues only consistent to third order. In our opinion one rather has to use an infinite partial summation that provides the poles and the residues on an equal footing. Such an infinite summation is discussed elsewhere (Cederbaum 1975b, Cederbaum and

Domcke 1977, Schirmer 1977). This infinite summation forms the basis for the approximation scheme used by our group to calculate outer valence ionisation potentials.

The preceding discussion also applies to the calculations presented by Purvis and Öhrn (1974) who build upon the super-operator approach of Pickup and Goscinski (1973). Although their approach is formally different from that of Simons and Smith, both methods are equivalent provided one makes use of the operator space h_1 , h_3 (Pickup and Goscinski 1973) in conjunction with the reference state of equation (46) (Jørgensen and Simons 1975). In actual calculations these authors, too, restrict themselves to diagonal and near-diagonal approximations with respect to the 2h1p (2p1h) excitations.

In conclusion we may say that from both a theoretical and a practical point of view the 2ph–TDA is a basic approximation scheme for the one-particle Green's function or related entities. This approximation has been shown to play a key role within several quite different approaches. In order to proceed one obviously has to start in one way or another from the 2ph–TDA. A rigorous application of this method will therefore be an essential step towards the development of more advanced approximations. The practical importance of the 2ph–TDA relies upon its applicability in realistic calculations. Such calculations for three diatomic molecules containing second-row atoms will be presented in the following paper.

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