Analysis of excitation energies and transition moments

Jens Oddershede, Poul Jørgensen and Nelson H F Beebe
Department of Chemistry, Aarhus University, DK-8000 Århus C, Denmark

Abstract. The lowest electronic transitions in H_2, CH^+ and Be have been analysed in terms of the individual contributions to excitation energies and transition moments in a second-order polarisation propagator calculation and in a second-order diagrammatic calculation based on both the full particle–hole propagator matrix and on the single-transition approximation. We found that collective effects, defined as sums of infinite series of irreducible self-energy diagrams, do not affect the excitation energies but change the intensities by up to 40 per cent. We further found that the cancellation effects among the second-order contributions to the excitation energy are substantial, indicating the importance of using methods which are consistent through a certain order in the electronic repulsion. Finally, we have shown that the single-excitation scheme is slowly convergent especially for systems with close-lying excited states.

1. Introduction

The concept *collective excitation* or *plasma oscillation* has been used in the theory of metals to denote an excitation which in an independent particle picture can be interpreted as originating from coherent (or collective) motion of many electrons. In the spectrum of a metal, a collective excitation usually shows up as an excitation with large intensity, well separated from other strong transitions (Hedin and Lundqvist 1969).

Transitions with similar characteristic spectral properties have been identified for atoms (Gelius 1974) and molecules and the notation 'collective excitations' has been used (Nicolaides and Beck 1976). These excitations do not, however, originate solely from 'collective motions' of many electrons and can be described in finite-order perturbation calculations (Nicolaides and Beck 1976).

Excitations of pure collective nature have so far not been identified in atomic and molecular spectra. In this communication we will investigate the effect of collective motion on already existing electronic transitions. We define the concept *collective effect* as the effect that coherent motion of many electrons has on an electronic transition which can be described in a finite-order perturbation theory. In a many-body language the present definition of collective effects corresponds to sums of infinite series of *irreducible* self-energy diagrams, e.g. the infinite series summed in the time-dependent Hartree–Fock (TDHF) approximation. Several other definitions of the concept 'collective effect' have been used in the literature (Amusia *et al* 1974, Wendin 1970, 1971, 1972, 1975, Lundqvist and Wendin 1974) and in §3 we return to a detailed comparison of the various definitions.

1

The analysis we will carry out is based on a polarisation propagator approach described by Oddershede and Jørgensen (1977a). We show how molecular and atomic transitions in the ultraviolet frequency range are affected by collective effects. We find that the collective effects originating from the TDHF series are important for an accurate description of the electronic transition moments whereas excitation energies are virtually unaffected. We have calculated excitation energies and transition moments which in addition to the collective effects contain all first- and second-order electronic correlation and we find that the importance of the collective effects is independent of the order of perturbation calculation. The effects we are discussing are thus of truly collective nature.

In a propagator calculation the electronic excitation energies are determined by diagonalising the proper particle–hole self-energy matrix (Oddershede and Jørgensen 1977a). An alternative and widely used approach consists of calculating only one excitation energy at a time (see e.g. Paldus and Čížek (1974)). We have calculated excitation energies using both methods and we find that through second order in electron repulsion, the approach based on the whole self-energy matrix gives much more reliable excitation energies, especially for close-lying excited states. We also examined the size of the individual contributions to the second-order excitation energies and found a considerable cancellation among second-order diagrams thus demonstrating the importance of using consistent theories.

In the next section we briefly discuss consistent approximations to the polarisation propagator and the particle–hole propagator based on the whole propagator matrix and on a single-transition approximation. We give a precise definition of the concept 'collective effect' and show how they can be separated from finite-order perturbation terms. In §3 numerical results are given for the lowest transition in Be, H_2 and CH^+ while §4 contains some concluding remarks.

2. Theory

2.1. The polarisation propagator

We use a finite basis set description. Let $\{u_i\}$ be a set of Hartree–Fock (HF) molecular orbitals and let a_i and $a_i^\dagger$ be the corresponding annihilation and creation operators. Indices $\alpha, \beta, \gamma, \delta$ (a, b, p, q) refer to orbitals which are occupied (unoccupied) in the HF ground state. The particle–hole creation operator is given as

$$q_{a\alpha}^\dagger = a_a^\dagger a_\alpha. \tag{1}$$

Using the notation of Zubarev (1960) and Linderberg and Öhrn (1973), the polarisation propagator matrix can be written as

$$P(E) = \begin{Bmatrix} \langle\!\langle \tilde{q}; q^\dagger \rangle\!\rangle_E & \langle\!\langle \tilde{q}; q \rangle\!\rangle_E \\ \langle\!\langle \tilde{q}^\dagger; q^\dagger \rangle\!\rangle_E & \langle\!\langle \tilde{q}^\dagger; q \rangle\!\rangle_E \end{Bmatrix} \tag{2}$$

where $q^\dagger = \{q_{m\alpha}^\dagger\}$ is a row vector and $\tilde{q}^\dagger$ is the transpose of $q^\dagger$. The spectral representation of the polarisation propagator (the particle–hole component) is

$$\langle\!\langle q_{a\alpha}; q_{b\beta}^\dagger \rangle\!\rangle = \lim_{\eta \to 0} \sum_n \left(\frac{\langle 0|q_{a\alpha}|n\rangle \langle n|q_{b\beta}^\dagger|0\rangle}{E - \omega_{0n} + i\eta} - \frac{\langle 0|q_{b\beta}^\dagger|n\rangle \langle n|q_{a\alpha}|0\rangle}{E + \omega_{0n} - i\eta} \right). \tag{3}$$

The poles for the propagator, $\pm\omega_{0n}$, are the exact excitation energies of the system and the residues give the corresponding transition moments.

In a previous publication (Oddershede and Jørgensen 1977a), we showed how the polarisation propagator could be obtained consistent through third order in the electronic repulsion in the form

$$P(E) = \left\{ \begin{matrix} E\mathbf{1} - A - \tilde{C}(E\mathbf{1} - D)^{-1}C & -B \\ -B & -E\mathbf{1} - A - \tilde{C}(-E\mathbf{1} - D)^{-1}C \end{matrix} \right\}^{-1}. \quad (4)$$

We have for convenience assumed that the matrices A, B, C, and D are real. Through first order in the electronic repulsion A and B are the standard RPA matrices involving only Hartree–Fock average values (Jørgensen 1975). In higher-order theories average values must be taken with respect to a correlated ground state (Oddershede and Jørgensen 1977a). The term $\tilde{C}(E\mathbf{1} - D)^{-1}C$ is the two-particle, two-hole correction and represents the effect of two-particle, two-hole excitations ($q^\dagger q^\dagger$) on the particle–hole ($q^\dagger$) spectrum (Jørgensen *et al* 1975). Using excitation operators of the proper spin symmetry, we can treat the singlet and triplet problems separately. The singlet–singlet and the singlet–triplet excitation spectra can be obtained from the singlet, $^1P(E)$, and the triplet, $^3P(E)$, propagators, respectively, both of which have the form given in equation (4). The explicit expressions for the matrices appearing in equation (4) are given by Oddershede and Jørgensen (1977a) and Oddershede *et al* (1977a). Oddershede and Jørgensen (1977a) also discuss the relation between the present approach and the configuration-interaction method. The order of the individual matrices A, B, C, and D necessary to obtain the polarisation propagator consistent through zeroth, first and second order in electron repulsion is summarised in table 1. In zeroth order the excitation energies are simple orbital-energy differences. The first-order approximation to the polarisation propagator represents the time-dependent Hartree–Fock approximation (Jørgensen 1975), which is identical to the random-phase approximation (RPA) with exchange. The second-order approximation is equivalent to the higher RPA method of Shibuya and McKoy (1970) and the self-consistent polarisation propagator approach of Linderberg *et al* (1972) both of which must be augmented with two-particle, two-hole (2p–2h) corrections (Shibuya *et al* 1973, Jørgensen *et al* 1975) to be consistent through second order (Oddershede and Jørgensen 1977a).

Table 1. The orders† of A, B, C and D matrices necessary to obtain the particle–hole and the polarisation propagator consistent through zeroth, first and second order in the electronic repulsion.

Order of propagator	Polarisation‡ propagator	Particle–hole§ propagator
(0)	$A(0)$	$A(0)$
(1)	$A(0), A(1), B(1)$	$A(0), A(1)$
(2)	$A(0), A(1), A(2)$	$A(0), A(1), A(2)$
	$B(1), B(2)$	$B(1), C(1), D(0)$
	$C(1), D(0)$	

† The number in parentheses indicates the orders of the matrices.
‡ With collective effects.
§ Without collective effects (equivalent to a diagrammatic perturbation expansion).

The polarisation propagator in equation (4) contains, in addition to terms which represent finite-order irreducible self-energy diagrams, infinite series of irreducible diagrams, i.e. collective effects (Oddershede and Jørgensen 1977a). This will become more apparent from the analysis of the particle–hole propagator in §2.2.

The propagator matrix in equation (4) is invariant under a transformation $E \rightarrow -E$ and is therefore consistent with a spectral representation (Linderberg and Öhrn 1973). This means that the transition-strength matrix elements $\langle n|q^{\dagger}|0\rangle$ and $\langle n|q|0\rangle$ can be determined from the residues of the particle–hole component of the polarisation propagator at the poles $E = \omega_{0n}$ and $E = -\omega_{0n}$, respectively (Jørgensen 1975). We have, however, shown (Oddershede *et al* 1977a) that through third order in the electronic repulsion, the transition strengths can alternatively be found from the full polarisation propagator in equation (4) by performing a pole search for positive E values alone. This procedure has been used to calculate the oscillator strengths reported in §3.

2.2. The particle–hole propagator

The particle–hole propagator is defined as the $\langle\!\langle \tilde{q}; \tilde{q}^{\dagger} \rangle\!\rangle_E$ component of the polarisation propagator and is obtained from the polarisation propagator by partitioning (Löwdin 1963) of the inverse matrix in equation (4)

$$\langle\!\langle \tilde{q}; q^{\dagger} \rangle\!\rangle_E^{-1} = E\mathbf{1} - A - \tilde{C}(E\mathbf{1} - D)^{-1}C - B[-E\mathbf{1} - A - \tilde{C}(-E\mathbf{1} - D)^{-1}C]^{-1}B. \tag{5}$$

The inverse matrices $(E\mathbf{1} - D)^{-1}$ and $[E\mathbf{1} + A - \tilde{C}(E\mathbf{1} + D)^{-1}C]^{-1}$ generate infinite series of diagrams each of which corresponds to individual terms in the expansion of the matrix

$$[E\mathbf{1} + A(0) + A(1)]^{-1} = [E\mathbf{1} + A(0)]^{-1} - [E\mathbf{1} + A(0)]^{-1}A(1)[E\mathbf{1} + A(0)]^{-1} + \dots. \tag{6}$$

The number in the parentheses following the matrices indicates the order of the matrices. For $B = B(1)$ we obtain the well known infinite sum of RPA ('ring') diagrams shown in figure 1 (Oddershede and Jørgensen 1977a). These diagrams can be interpreted as repeated particle–hole scattering events. The RPA series of diagrams are the only infinite series present in the first-order theory for the polarisation propagator (TDHF-like approach). In a second-order TDHF-like approach where $B = B(1) + B(2)$ and $A = A(1) + A(2)$ (see table 1) other RPA-like infinite series appear. These series show up when a $B(1)$ matrix element is replaced by a $B(2)$ element and when an $A(1)$ element is replaced by an $A(2)$ or a $\tilde{C}(1)[E\mathbf{1} + D(0)]^{-1}C(1)$ matrix element or a combination of both. All these series can still be characterised as partly representing repeated particle–hole-type scattering.
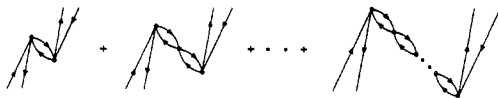
Figure 1. The infinite RPA series of irreducible diagrams which originate from the expansion of the inverse matrix in the term $B(1)[E + A(0) + A(1)]^{-1}B(1)$ in the proper particle–hole self energy. A dot represents an antisymmetrised vertex (Hugenholtz 1957).

In a third order TDHF-like theory more complicated RPA-like series will be generated by the last term in equation (5). The D matrix then includes first-order terms and the $(E\mathbf{1} - D)^{-1}$ matrix introduces additional infinite series of irreducible diagrams. We refer to our previous paper (Oddershede and Jørgensen 1977a) for a closer analysis of these series of diagrams.

The polarisation propagator approach thus implicitly includes irreducible diagram series summed to infinite order. Kelly (1969) refers to these summations of diagrams as energy shifted denominators. In an order-by-order evaluation of the particle–hole propagator, these infinite series of diagrams are not included. The expressions for the propagator in a strict diagrammatic approach can be derived from the particle–hole propagator in equation (5) by neglecting certain terms. The matrix elements needed to obtain the particle–hole propagator consistent through first and second order in the electronic repulsion are listed in table 1. If we write equation (5) in the form

$$\langle\!\langle \tilde{q}^{\dagger}; q \rangle\!\rangle_{E}^{-1} = E\mathbf{1} - A(0) - M(E) \tag{7}$$

where $M(E)$ is the proper particle–hole self-energy or Bethe–Salpeter kernel, it follows from table 1 that in a *strict* first-order theory the self energy is

$$M^{(1)}(E) = A(1). \tag{8}$$

This represents the single-excited configuration interaction (SECI) or the Tamm–Dancoff approximation. In a *strict* second-order diagrammatic approach the self energy is (see table 1)

$$M^{(2)}(E) = M^{(1)}(E) + A(2) + \tilde{C}(1)[E\mathbf{1} - D(0)]^{-1}C(1) + B(1)[-E\mathbf{1} - A(0)]^{-1}B(1) \tag{9}$$

which can be obtained from the second-order TDHF-like approach by discarding the $B(2)$, $A(1)$, $A(2)$ and $\tilde{C}(1)[E\mathbf{1} - D(0)]^{-1}C(1)$ matrices in the last term in equation (5). This approximation is expected to have a minor effect on the poles located at positive E values, whereas the positions of the negative poles change more drastically due to the fact that the asymptotes in the *negative* energy plane in the second-order diagrammatic approach appear at $E\mathbf{1} + A(0) = 0$ (see equation (9)) and at $E\mathbf{1} + A(0, 1, 2) + \tilde{C}(1)[-E\mathbf{1} - D(0)]^{-1}C(1) = 0$ in the TDHF-like approach (see equation (5)). The self energy in equation (9) is no longer invariant under the transformation $E \rightarrow -E$ and the corresponding particle–hole propagator can consequently not be represented in the normal spectral form (3). The determination of transition moments requires, as stated in §2.1, in principle knowledge of the residues for both $E = \omega_{0n}$ and the corresponding pole in the negative plane.

A closer analysis of the self energy in equation (9) shows, however, that in a *second*-order diagrammatic approach it is possible to obtain the transition moment from the positive E solutions alone. In figure 2 we have displayed the behaviour of the lowest eigenvalues of $M^{(2)}(E)$ for Be. The values of the lowest positive and negative excitation energies are also indicated. The negative poles are located close to the asymptotes in the region where the descent of $\omega(E)$ is very steep. The factor

$$\Gamma = [1 - (d\omega(E)/dE)_{E = -\omega_{0n}}]^{-1}$$

is thus very small (equal to about -5×10^{-3} for the least negative pole in figure 2). Oddershede *et al* (1977a) have shown that for energy-dependent self energies, such as $M^{(2)}(E)$ in equation (9), the eigenvectors from the RPA-like eigenvalue problem (for $E = -\omega_{0n}$) must be multiplied by Γ to obtain the transition-strength matrix
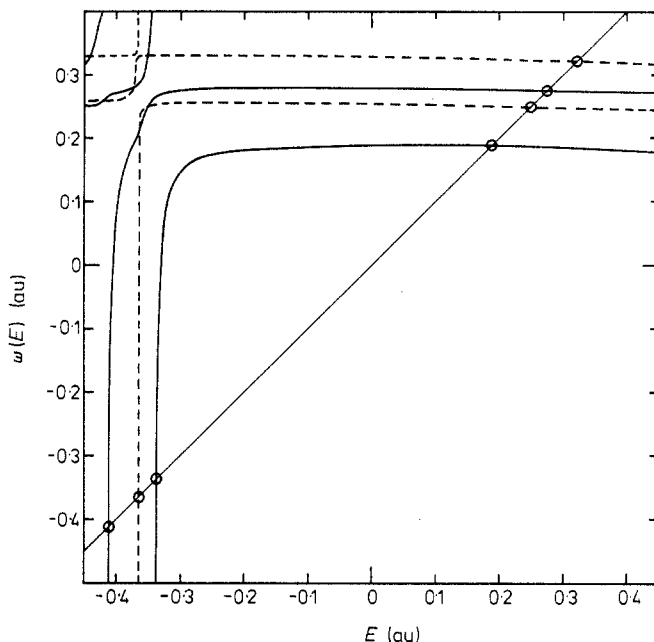
Figure 2. The two lowest eigenvalues of pi symmetry (full curves) and of sigma symmetry (broken curves) for the self-energy matrix in the second-order diagrammatic perturbation calculation for Be as a function of the energy parameter E. The excitation energies are the points for which $E = \omega(E)$ (see equation (7)) and are marked with circles.

element corresponding to $-\omega_{0n}$, $\langle n|q|0\rangle$. Since the eigenvectors are of similar magnitude for $E = \pm \omega_{0n}$, the smallness of Γ for $E = -\omega_{0n}$ shows that $\langle n|q|0\rangle$ can be neglected compared with $\langle n|q^\dagger|0\rangle$ in the second-order diagrammatic approach. In higher orders the behaviour of $M(E)$ for negative E values will be different and the present conclusion may not hold.

Knowing the A, B, C, and D matrix elements, we can calculate excitation energies and transition moments from the particle–hole propagator consistent through a certain order, and from comparison with the polarisation propagator calculated through the same order, we obtain a measure of the significance of the collective effects present in the polarisation propagator approach. The importance of the collective effects originates from the very different behaviour of the self energy for negative energies in a strict-order diagrammatic approach and in the corresponding polarisation propagator method. A much higher level of approximation than the second- and third-order theories considered here is required if the self energy in a strict-order diagrammatic approach which does not include collective effects is to attain the proper behaviour of the self energy for negative E values.

2.3. Single-excitation part of the particle–hole propagator

In the preceding analysis we have assumed that the excitation energies are obtained by diagonalising the whole $M(E)$ matrix. In most diagrammatic perturbation calculations, however, only one excitation ($m\alpha$) is considered at a time (Paldus and Čížek 1974). This means that only the diagonal elements in $\langle\!\langle \tilde{q}; q^\dagger \rangle\!\rangle_E$ are computed.
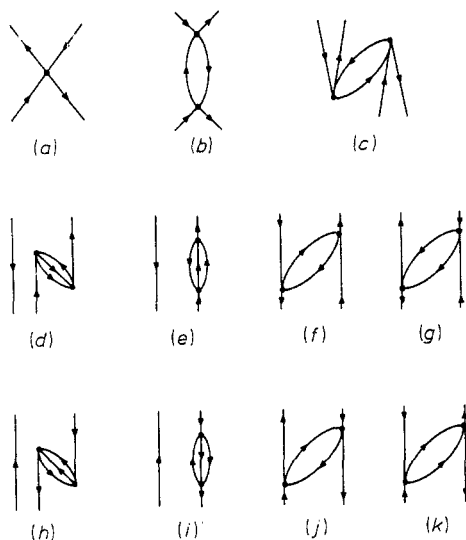
Figure 3. All irreducible first (a) and second (b)–(k) single-excitation self-energy diagrams. In a particle–hole propagator calculation figure 3(b) is reducible.

According to table 1 the first-order compact vertex part in the single-excitation-type perturbation calculation is the diagonal part of $A(1)$, i.e.

$$M_{SE}^{(1)}(E)_{m\alpha,m\alpha} = A(1)_{m\alpha,m\alpha} \tag{10}$$

which is diagrammatically represented in figure 3(a). This approximation corresponds to a single determinantal energy difference and is often referred to as the virtual Hartree–Fock or single-transition approximation (STA) (see e.g. Dunning and McKoy 1967).

In second order $M_{SE}(E)$ consist of the diagonal elements of $M^{(2)}(E)$ plus one additional term originating from partitioning of the effect of all other $A(1)$ matrix elements into the $A_{m\alpha,m\alpha}$ element. This element can be analytically represented by

$$\delta M_{m\alpha,m\alpha}^{(2)} = - \sum_{n\beta \neq m\alpha} A(1)_{m\alpha,n\beta}(E - A(0)_{n\beta,n\beta})^{-1} A(1)_{n\beta,m\alpha} \tag{11}$$

and the corresponding Hugenholtz (1957) diagram (see also Brandow 1967) is displayed in figure 3(b). This diagram is reducible in the diagrammatic approach where we diagonalise the whole $M(E)$ matrix (Oddershede and Jørgensen 1977a) but is irreducible in a single-excitation perturbation calculation (Paldus and Čížek 1974). In a second-order single-excitation approach the total proper particle–hole self energy thus becomes

$$M_{SE}^{(2)}(E)_{m\alpha,m\alpha} = M^{(2)}(E)_{m\alpha,m\alpha} + \delta M_{m\alpha,m\alpha}^{(2)}. \tag{12}$$

The corresponding Hugenholtz diagrams are displayed in figure 3. It can be shown (Oddershede and Jørgensen 1977b) that the excitation energy computed from $M_{SE}^{(2)}$ contains all pair correlation and orbital relaxation effects through second order in the electronic repulsion. Comparison of excitation energies obtained from the

particle–hole propagator and from the single-excitation approach gives information about the importance of off-diagonal elements in the self-energy matrix.

3. Results

3.1. General remarks

We calculated excitation energies and oscillator strengths in the dipole length and dipole velocity approximation using the three different methods described in the preceding section: the polarisation propagator approach which includes collective effects, the diagrammatic or particle–hole propagator method which through second order does *not* contain collective effects and the single-excitation scheme. Results through first and second order in the electronic repulsion are given in tables 2–4. The electronic transition moments are, together with the excitation energies, displayed in figures 4–6. For H_2 we used a basis set consisting of 38 Slater-type orbitals (STO) and for CH^+ a 45 STO basis set was used (see Oddershede *et al* 1977b for details). For Be we used the basis set given by Moser *et al* (1976) (50 STO). With basis sets of the indicated size the errors due to use of finite basis sets are very small. To obtain a numerical estimate of the magnitude of this error, we have performed another calculation on Be using a 38 STO basis set. The basis set consisted of two 1s and 3p functions, four 2s and 2p functions, and one 3s, 4p, 3d and 4d function and is thus quite different from the basis set used by Moser *et al* (1976). The exponents were in general substantially larger than those given by Moser *et al* (1976). We found, in agreement with previous experience (Oddershede and Elander 1976, Elander *et al* 1977), that the transition moments were least affected by the change in basis set. The excitation energies differed by 1 to 3% whereas the change in the transition moments were below 1%. Both error bars are, however, well below the size of the effects that we are calculating in the present communication.

Table 2. Excitation energies (ϵ) and oscillator strengths in the dipole length (f_L) and the dipole velocity (f_V) formulation for the $X\,^1\Sigma_g^+$ to $B\,^1\Sigma_u^+$ transition in H_2 at $R = 1\cdot40$ Bohr.

	ϵ (eV)	f_L	f_V
Single-excitation scheme			
1st order (STA, HF)	14·26	0·088	0·032
2nd order	13·87		
Diagrammatic without collective effects			
1st order (SECI)	12·73	0·307	0·228
2nd order	12·70	0·323	0·246
Polarisation propagator with collective effects			
1st order (TDHF, RPA)	12·67	0·285	0·288
2nd order (SOPPA)	12·69	0·289	0·292
2nd order with shifted denominator	12·82	0·298	0·297
Other results			
RPA results†	12·67	0·293	
Kolos and Wolniewicz	12·75‡	0·300§	0·307§

† R F Stewart, D K Watson and A Dalgarno 1976 *J. Chem. Phys.* **65** 2104–11.
‡ Kolos and Wolniewicz (1965, 1968).
§ Wolniewicz (1969).

Table 3. Excitation energies (ϵ) and oscillator strengths in the dipole length (f_L) and the dipole velocity (f_V) formulation for the $X\,^1\Sigma^+$ to $A\,^1\Pi$ transition in CH^+ at $R = 2.137$ Bohr.

	ϵ (eV)	f_L	f_V
Single-excitation scheme			
1st order (HF, STA)	3.60	0.0537	0.0724
2nd order	3.21		
Diagrammatic without collective effects			
1st order (SECI)	2.87	0.0224	0.0144
2nd order	2.98	0.0237	0.0072
Polarisation propagator with collective effects			
1st order (TDHF, RPA)	2.60	0.0111	0.0167
2nd order (SOPPA)	2.87	0.0120	0.0131
2nd order with shifted denominator	2.72	0.0110	0.0137
Other results			
RPA results†	2.39	0.0109	
CI	3.17‡	0.0147§	
Experiment‖	3.07		

† D K Watson, R F Stewart and A Dalgarno 1976 *J. Chem. Phys.* **64** 4995–9.
‡ S Green, P S Bagus, B Liu, A D McLean and M Yoshimine 1972 *Phys. Rev.* A **5** 1614–8.
§ M Yoshimine, S Green and P Thaddeus 1973 *Astrophys. J.* **183** 899–902 (interpolated value).
‖ Calculated from the experimental RKR curves for the $X\,^1\Sigma^+$ and $A\,^1\Pi$ states given by I Botterud, A Lofthus and L Veseth 1973 *Phys. Scr.* **8** 218–24.

For H_2 our calculated excitation energy and oscillator strengths agree well with those calculated by Kolos and Wolniewicz (1965, 1968) and Wolniewicz (1969). For Be satisfactory agreement is obtained with the experimental oscillator strength (Martinson *et al* 1974) and excitation energy (Moore 1949) even though the agreement was not as good as that obtained by Moser *et al* (1976) using the *same* basis set.

Table 4. Excitation energies (ϵ) and oscillator strengths in the dipole length (f_L) and the dipole velocity (f_V) formulation for the $1s^2 2s^2(^1S)$ to $1s^2 2s 2p(^1P)$ transition in Be.

	ϵ (eV)	f_L	f_V
Single-excitation scheme			
1st order (STA, HF)	5.36	1.52	0.73
2nd order	5.55		
Diagrammatic without collective effects			
1st order (SECI)	5.04	1.92	0.88
2nd order	5.10	1.96	0.86
Polarisation propagator with collective effects			
1st order (TDHF, RPA)	4.79	1.39	1.38
2nd order (SOPPA)	5.02	1.43	1.28
2nd order with shifted denominator	· 4.96	1.42	1.30
Other results			
Bethe–Goldstone†	5.29	1.39	1.38
Experiments	5.28‡	1.34 ± 0.05§	

† Moser *et al* (1976).
‡ Moore (1949).
§ Martinson *et al* (1974).
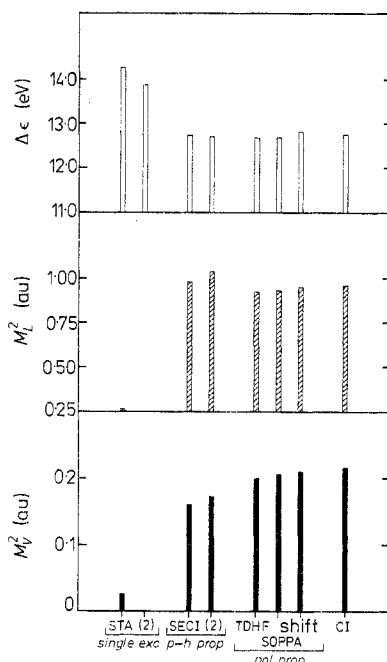
Figure 4. Excitation energies (ΔE) and the square of the electronic transition moments in the dipole length (M_L^2) and the dipole velocity (M_V^2) formulation for the x $^1\Sigma_g^+ \rightarrow$ B $^1\Sigma_u^+$ transition in H_2 ($R = 1\cdot40$ Bohr) calculated at different levels of approximation: (i) single-excitation perturbation calculation (*single exc*) in first order (STA) and second order (2) respectively; (ii) diagrammatic perturbation calculation without collective effects (*p–h prop*) in first order (SECI) and second order (2) respectively; (iii) polarisation propagator calculation with collective effects (*pol prop*) in first order (TDHF), second order (SOPPA) and second order with energy-shifted denominators (shift). Comparisons are made with the CI calculations of Kolos and Wolniewicz (1965, 1968) and Wolniewicz (1969).

This indicates that higher-order propagator methods are needed to remove the residual disagreement between theory and experiment (Oddershede *et al* 1977a, Jørgensen *et al* 1977). The electronic oscillator strength is not a directly measurable quantity for molecules (see e.g. Hinze *et al* 1975, Oddershede and Elander 1976) and direct comparison with experiments is only possible through the use of the electronic transition moment to calculate radiative lifetimes. This has been done for CH^+ using the present method (Elander *et al* 1977) and we found very good agreement between experimental and theoretical radiative lifetimes.

In the next three subsections we will discuss some common features of the spectra in figures 4–6 and tables 2–4.

3.2. Collective effects

The difference between the polarisation and particle–hole propagator results in figures 4–6 indicates the importance of the collective effects. It is evident from the three examples that inclusion of collective effects (the polarisation propagator approach) improves the quality of the electronic transition moments both in the length and velocity approximation, whereas the influence on the excitation energies as expected is negligible. The largest effect is found for Be and the smallest for
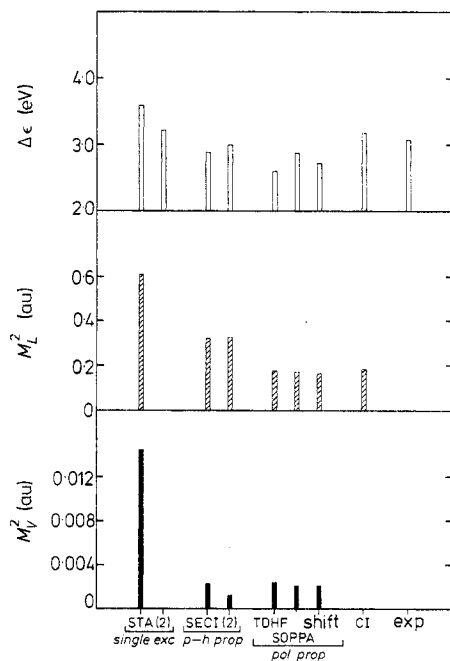
Figure 5. The X $^1\Sigma^+ \rightarrow$ A $^1\Pi$ transition in CH$^+$ at $R = 2\cdot137$ Bohr. See caption for figure 4 and table 3 for explanation of the abbreviations.
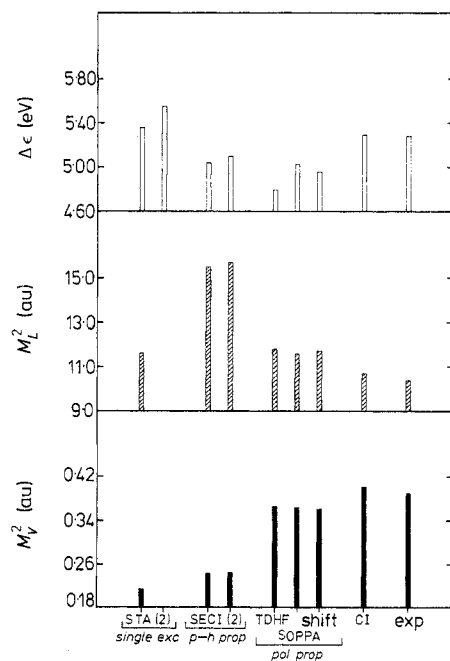
Figure 6. The $1s^2 2s^2(^1S) \rightarrow 1s^2 2s2p(^1P)$ transition in Be. See caption for figure 4 and table 4 for explanation of the abbreviations.

H_2 in agreement with the general observation that correlation effects are much more important for Be than for H_2.

Another important feature can be observed from figures 4–6. The importance of the collective effects depends very little on whether they are added to a first- or second-order calculation. The differences between SECI and TDHF results are almost the same as the differences between the corresponding second-order results. In other words, the contribution to the transition moments from the second-order RPA diagram in figure 3(c) is unimportant, whereas the summed contribution from the *whole* RPA series is substantial. This conclusion is apparently in disagreement with the observation made by Kelly and Simons (1973) who find that the RPA terms beyond second order can be neglected. Kelly and Simons used a V^{N-1} potential, whereas we use a V^N potential for the virtual Hartree–Fock orbitals which is probably the reason for the slow convergence of our RPA series (Kelly 1963).

The lack of a common precise definition of the concept 'collective effect' has previously caused some confusion. One such example is the calculation of the ionisation of the 4d subshell of Ba I. Wendin (1973) found that collective effects as calculated in the random-phase approximation (RPA) with exchange were very important for the description of the 4d photoabsorption in Ba, whereas Fliflet *et al* (1974) concluded that the absorption was described equally well in the Hartree–Fock and in the RPA level of approximation. This apparent disagreement was caused by a different choice of the V^{N-1} potentials. Part of the correlation included in the V^{N-1} potential of Fliflet *et al* (1974) was denoted collective effects by Wendin (1975) and estimates of the collective effects in the two calculations were thus quite different. Brandt and Lundqvist (1963, 1965, 1967) and Wendin (1970, 1971, 1972, 1975) denote all correlation not present in a one-electron description, based on a V^{N-1} potential, as collective effects, provided the correlation gives an appreciable shift in the transition described in the one-electron picture. All correlation corresponding to summing *Green's* function diagrams to infinite order is thus denoted collective by Wendin (1975). With this definition the correlation included in the Tamm–Dancoff approximation will be denoted collective and many of the terms included in the V^{N-1} potential used by Fliflet *et al* (1974) are hence denoted collective by Wendin.

3.3. Single-excitation calculations

Comparison of excitation energies in the single-excitation scheme and those obtained from the poles of the particle–hole propagator shows that the latter approach gives more reliable excitation energies for H_2 and Be. For CH^+ the excitation energies are of comparable quality, due to the fact that the x $^1\Sigma^+ \to$ A $^1\Pi$ transition is well separated from other transitions of the same symmetry. For H_2 and Be, this is not the case, and it is therefore important to incorporate the effect of off-diagonal matrix elements in $M(E)$ in a non-perturbative manner as done in the particle–hole propagator approach where the excitation energies are obtained from diagonalising the whole $M(E)$ matrix.

If the single-excitation calculation is carried to sufficiently high order in electron repulsion, it will give the same answer as the diagonalisation procedure. The single-excitation scheme is thus a slowly convergent procedure. This conclusion agrees with that reached by Paldus and Čížek (1974). It should in this connection be noted that use of the V^{N-1} potential would probably have resulted in a better convergence in the single-excitation calculation (Kelly 1969).

3.4. Cancellation effects

In table 5 we have listed the individual second-order contributions to the Be 2s–2p excitation energy as calculated from the particle–hole propagator. Even though some of the individual terms are rather large, the total contribution from all second-order diagrams is modest, due to cancellation effects between individual diagrams. This behaviour was found for all the calculated excitation energies.

Table 5. Second-order contribution to the excitation energy for the $1s^2 2s^2 (^1S)$–$1s^2 2s 2p (^1P)$ transition in Be.

Contributions from:	Diagrammatic representation	$\Delta\epsilon$ (eV)
Reference-state correlation	Figures 3(d)–(e)	+0·92
RPA term	Figure 3(c)	−0·16
2p–2h terms	Figures 3(f)–(k)	−0·70
All 2nd-order terms	Figures 3(c)–(k)	+0·06

The diagrams in figures 3(d) and (e) represent $A(2)$ matrix elements, i.e. the second-order contribution to the excitation energy originating from using a correlated ground state (Oddershede and Jørgensen 1977a). These two diagrams give a large positive contribution to the excitation energy. They are the only extra diagrams included in the higher RPA scheme by Shibuya and McKoy (1970) and the self-consistent polarisation propagator approximation (Linderberg et al 1972), both of which are known to give too large excitation energies (Rose et al 1973, Jørgensen et al 1974). These methods must be augmented with the effect of two-particle, two-hole excitations (2p–2h) to give reliable excitation energies (Rose et al 1973, Oddershede et al 1975). The 2p–2h terms (the $\tilde{C}(E1 - D)^{-1}C$ matrix in equation (4)) are diagrammatrically represented in figures 3(f)–(k) and the numbers in table 5 clearly show the above-mentioned cancellation effects between the 2p–2h terms and the rest of the second-order contributions.

The analysis demonstrates that reliable results can only be expected from the consistent second-order approach. Inclusion of either 2p–2h terms or reference-state correlation alone gives unreliable excitation energies.

4. Conclusions

We have used second-order propagator approaches to analyse the lowest transitions in Be, H_2 and CH^+. We found that collective effects, defined as sums of infinite series of irreducible particle–hole self-energy diagrams, contributed very little to excitation energies but were extremely important for a reliable description of the intensities of the spectra. The RPA series was especially important. We found that inclusion of RPA diagrams in first as well as second order improved the agreement between the oscillator strengths in the dipole length and the dipole velocity formulation. In a first-order theory (TDHF) the length and velocity formulations are equivalent if we use a complete basis set (Harris 1969).

In a second-order diagrammatic approach we have shown that there is a considerable cancellation among the individual diagrammatic contributions in agreement with

the finding by Yeager and Freed (1977). This demonstrates the importance of using consistent theories to calculate excitation spectra.

For Be and H_2 we found that the second-order excitation energies calculated in a single-excitation perturbation calculation are less accurate than those obtained from the poles of the whole particle–hole propagator matrix. In CH^+ where the lowest state is well separated from other states with the same symmetry, the two propagator approaches give excitation energies of comparable quality.

As a final comment we would like to add that all the above conclusions are based on a few calculations on smaller atoms and molecules. Further applications on large systems are necessary. We do not expect that the cancellation effects and the slow convergence of the single-excitation calculation will be less pronounced in larger systems. The importance of collective effects will probably increase, especially for systems with populated d and f shells. This latter point would be in agreement with the conclusion reached by Wendin (1974).

Acknowledgments

References

Amusia M Ya, Cherepkov N A, Janev R K and Zivanović Dj 1974 *J. Phys. B: Atom. Molec. Phys.* **7** 1435–50
Brandow B H 1967 *Rev. Mod. Phys.* **39** 771–828
Brandt W and Lundqvist S 1963 *Phys. Rev.* **132** 2135–43
——1965 *Ark. Fys.* **28** 399–414
——1967 *J. Quant. Spectrosc. Radiat. Transfer* **7** 911–21
Dunning T H and McKoy V 1967 *J. Chem. Phys.* **47** 1735–47
Elander N, Oddershede J and Beebe N H F 1977 *Astrophys. J.* **216** 165–73
Fliflet A W, Chase R L and Kelly H P 1974 *J. Phys. B: Atom. Molec. Phys.* **7** L443–6
Gelius U 1974 *J. Electron Spectrosc.* **5** 985–1057
Harris R A 1969 *J. Chem. Phys.* **50** 3947–51
Hedin L and Lundqvist S 1969 *Solid St. Phys.* **23** 1–181 ed F Seitz, D Turnbull and H Ehrenreich (New York: Academic Press)
Hinze J, Lie G C and Liu B 1975 *Astrophys. J.* **196** 621–31
Hugenholtz N M 1957 *Physica* **23** 481
Jørgensen P 1975 *Ann. Rev. Phys. Chem.* **26** 359–80
Jørgensen P, Oddershede J, Albertsen P and Beebe N H F 1977 *J. Chem. Phys.* to be published
Jørgensen P, Oddershede J and Ratner M 1974 *J. Chem. Phys.* **61** 710–8
——1975 *Chem. Phys. Lett.* **32** 111–5
Kelly H P 1963 *Phys. Rev.* **131** 684–99
——1969 *Adv. Chem. Phys.* **14** 129–90
Kelly H P and Simons G 1973 *Phys. Rev. Lett.* **30** 529–32
Kolos W and Wolniewicz L 1965 *J. Chem. Phys.* **43** 2429–41
——1968 *J. Chem. Phys.* **48** 3672–80
Linderberg J, Jørgensen P, Oddershede J and Ratner M 1972 *J. Chem. Phys.* **56** 6213–9
Linderberg J and Öhrn Y 1973 *Propagators in Quantum Chemistry* (London: Academic Press)
Löwdin P-O 1963 *J. Molec. Spectrosc.* **10** 12–33
Lundqvist S and Wendin G 1974 *J. Electron Spectrosc.* **5** 513–28
Martinson I, Gaupp A and Curtis L J 1974 *J. Phys. B: Atom. Molec. Phys.* **7** L463–5

Moore C E 1949 *Atomic Energy Levels* NBS Circular No 467 (Washington DC: US Govt Printing Office)

Moser C M, Nesbet R K and Gupta M N 1976 *Phys. Rev.* A **13** 17–22

Nicolaides C A and Beck D R 1976 *J. Phys. B: Atom. Molec. Phys.* **9** L259–63

Oddershede J and Elander N 1976 *J. Chem. Phys.* **65** 3495–505

Oddershede J and Jørgensen P 1977a *J. Chem. Phys.* **66** 1541–55

——1977b *Chem. Phys. Lett.* **47** 61–4

Oddershede J, Jørgensen P and Beebe N H F 1975 *J. Chem. Phys.* **63** 2996–3007

——1977a *Int. J. Quantum Chem.* in press

——1977b *Chem. Phys.* in press

Paldus J and Čížek J 1974 *J. Chem. Phys.* **60** 149–63

Rose J, Shibuya T-I and McKoy V 1973 *J. Chem. Phys.* **58** 74–83

Shibuya T-I and McKoy V 1970 *Phys. Rev.* A **2** 2208–16

Shibuya T-I, Rose J and McKoy V 1973 *J. Chem. Phys.* **58** 500–7

Wendin G 1970 *J. Phys. B: Atom. Molec. Phys.* **3** 466–77

——1971 *J. Phys. B: Atom. Molec. Phys.* **4** 1080–95

——1972 *J. Phys. B: Atom. Molec. Phys.* **5** 110–32

——1973 *Phys. Lett.* **46A** 119–20

——1974 *Proc. 4th Int. Conf. on VUV Radiation Physics* ed E-E Koch, R Haenzel and C Kunz (Braunschwieg: Pergamon/Vieweg) pp 225–39

——1975 *Phys. Lett.* **51A** 291–2

Wolniewicz L 1969 *J. Chem. Phys.* **51** 5002–8

Yeager D L and Freed K F 1977 *Chem. Phys.* **22** 415–33

Zubarev D N 1960 *Usp. Fiz. Nauk.* **71** 71–116 (*Sov. Phys.-Usp.* **3** 320–45)