

## Direct calculation of energy differences, such as ionization potentials

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**Abstract.** 'Indirect' methods for the calculation of energy differences imply that two separate calculations of the involved states are performed first and then the difference is taken. In a 'direct' method the transition energy is calculated without an attempt to calculate either of the states between which transition takes place. The theory of direct calculations of energy differences is reviewed with emphasis on ionization potentials and special attention to the method of a common unitary transformation of two model states. Results for the ionization potentials of a few small molecules are presented. The elements of a more general theory are outlined in which the Liouvillean superoperator (and its resolvent) as well as the Fock space formulation of quantum chemistry (especially the concept of effective Hamiltonians in Fock space) play a key role.

**Keywords.** Energy differences; ionisation potentials; cluster expansion; electron correlation; Liouville operator; Fock space; effective Hamiltonians; Green's function.

### 1. Introduction

It is not too difficult to calculate the absolute energy of the ground state (or a low-lying excited state) of an atom or a molecule with an error of less than about 1%. Unfortunately, the quantities of physical or chemical interest are not absolute energies, but rather are energy differences, such as binding energies or spectral transition energies. The order of magnitude of these differences is often comparable to the order of magnitude of the errors of the respective absolute energies, such that it is not easy to evaluate these energy differences with sufficient accuracy because one needs to compute the two states in a 'balanced' way.

That this 'indirect' way of the calculation of ionization potentials (IP) can lead to satisfactory results if a sufficiently sophisticated approach is used, has probably been first shown by Meyer (1971, 1973) for the IP of H<sub>2</sub>O and CH<sub>4</sub> using the PNO-CI and CEPA-PNO methods.

Methods that lead directly to ionization potentials and transition energies, not as small differences between large numbers, should nevertheless be both more economic and more reliable since contributions to the two states which cancel in the difference need not be evaluated at all.

The simplest approach towards a direct calculation of ionization potentials is due to Koopmans (1933). It is based on two assumptions:

(a) one can describe a molecule in its ground state by a Slater determinant  $\Phi$  constructed from (doubly occupied) Hartree-Fock orbitals,

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Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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(b) the wave function of the ion is obtained by occupying one orbital in the ground state Slater determinant singly rather than doubly, without changing the orbitals.

It follows from these two assumptions that the ionization potential  $I_i$  is (except for the sign) equal to the Hartree-Fock orbital energy  $\varepsilon_i$  of the orbital  $\varphi_i$  from which one has removed one electron

$$I_i = -\varepsilon_i; F\varphi_i = \varepsilon_i\varphi_i. \quad (1)$$

Koopmans' theorem is often valid to a good degree of approximation, even if the two assumptions (a) and (b) are hardly justified. Mulliken (1949) was probably the first to realize that Koopmans' theorem is based to a large extent on a compensation of two errors. Koopmans' assumption (b) is certainly wrong; on removal of one electron from the orbital  $\varphi_i$  the remaining orbitals 'relax', i.e. they adjust to the change in the potential. This relaxation lowers the energy of the ion. The  $\varepsilon_i$  should hence overestimate the  $I_i$  (see figure 1).

However, assumption (a) is also not fully correct. Electron correlation lowers the energy as compared to that of a single Slater determinant. This energy lowering is usually larger for a larger number of electrons, i.e. it is larger for the neutral molecule than for the ion. As one sees from figure 1 relaxation and change in correlation energy have usually opposite signs and compensate each other to a large extent.

Mulliken (1949) has also been able to show that Koopmans' theorem is very poor for electron affinities. As one sees from figure 2 the errors due to relaxation and change in the correlation energy have the same sign and do not cancel. The Koopmans value may even have the wrong sign. If one looks at this problem more carefully one also realizes that the energies of unoccupied orbitals are (at variance with those of occupied orbitals) not well defined and basis-dependent such that the Koopmans value for an electron affinity is rather meaningless.

Most more sophisticated direct methods for ionization potentials have in common that they contain Koopmans' approach as the zeroth order step. Direct methods for the calculation of spectral transition energies are closely related. In either case one is interested in the difference of eigenvalues of one Hamiltonian (that has to be interpreted in Fock space for ionization potentials). Unfortunately there is no really promising approach towards a direct calculation of binding energies, because here one has to deal with eigenvalues of different Hamiltonians.

The existing direct methods can be roughly classified as follows

- (a) perturbation-theoretical (Malrieu 1967; Chong *et al* 1974; Kvasnicka and Hubac 1974; Lindgren 1974; Kaldor 1975a, b; Hose and Kaldor 1979)
- (b) non-perturbative (coupled cluster type) (Mukherjee *et al* 1975, 1977; Offermann *et*

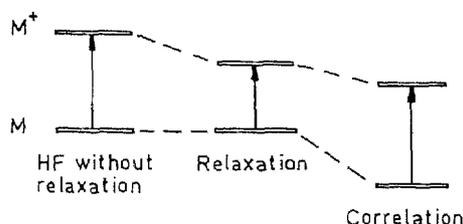


Figure 1. Illustration of Koopmans' theorem for ionization potentials.

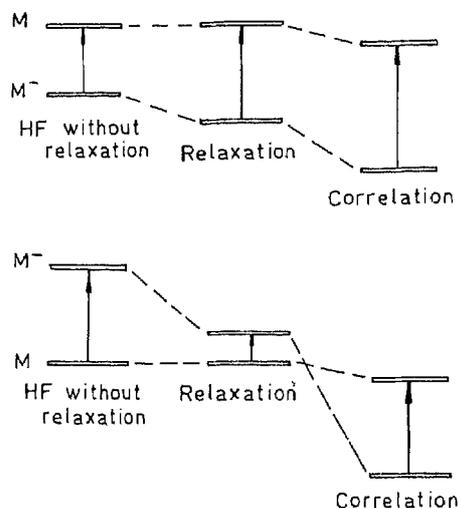


Figure 2. Illustration of Koopmans' theorem for electron affinities.

*al* 1976; Monkhorst 1977; Harris 1977; Lindgren 1978; Paldus *et al* 1978; Nakatsuji 1978, 1979; Mukherjee 1979; Mukherjee and Mukherjee 1979; Emrich 1981; Kvasnicka 1981; Jeziorski and Monkhorst 1981; Haque and Mukherjee 1984)

(c) variational or quasi-variational (Westhaus and Bradford 1975; Kutzelnigg 1977; Reitz and Kutzelnigg 1979; Pal *et al* 1984)

(d) based on Green's functions or propagators (Rowe 1968; Dunning and McKoy 1967, 1968; Doll and Reinhardt 1972; Ecker and Holneicher 1972; Cederbaum 1973; Pickup and Goscinski 1973; Simons and Smith 1973; Purvis and Öhrn 1974; Cederbaum and Domcke 1977; Linderberg and Öhrn 1977; Herman *et al* 1977; Oddershede 1978; Öhrn and Born 1981; Schirmer 1982; Schirmer *et al* 1983).

One should note, however, that the Green's function methods also use perturbation theory; non-perturbative Green's function methods have only been proposed recently (Oddershede 1978; Öhrn and Born 1981; Schirmer 1982; Schirmer *et al* 1983). There are further methods that have their origin in simplifications of Green's functions methods, but that can be formulated without referring to Green's functions, such as the RPA (random-phase approximation) or EOM (equations of motions) methods (Rowe 1968; Dunning and McKoy 1967, 1968; Simons and Smith 1973; Herman *et al* 1977; Linderberg and Öhrn 1977).

We do not intend to give a comprehensive review of the subject, we rather concentrate on work of the present authors. Our interest in the direct calculation of energy differences has started with the method of Reitz and Kutzelnigg (1979) that is based on a common unitary transformation of two model states. This method is formally simple and transparent and does not require more effort than perturbation theory to 3rd order—although it is usually quite superior to perturbation theory. It also provides a straightforward analysis of the various corrections to the Koopmans energies. We review this method in §2 and give there also a few results that have so far not been published.

We shall not hide cases where this method is less satisfactory and we shall discuss possible improvements and generalization in §3. This method already contains two ingredients that are essential for a theory of energy differences, namely the central role of a Liouvillean operator and of a Fock space formulation. These concepts will be outlined more generally in §§4, 5 and 7, while §6 is devoted to the concept of effective Hamiltonians in Fock space that allows the most straightforward access to energy differences even in the case of near degeneracies. At the end of §7 the relation of our formalism to that of one-particle Green's functions and propagators in general is briefly mentioned.

## 2. A common unitary transformation of two model states (Reitz and Kutzelnigg 1979)

Let the neutral ground state be of a closed-shell type such that it can be described to a good degree of approximation by a single Slater determinant 'model wave function'  $\Phi$ . An approximate wave function  $\Phi'$  of an excited (or ionized) state can then be constructed from  $\Phi$  by means of a 'model excitation' (or 'model ionization') operator  $\Omega^+$

$$\Phi' = \Omega^+ \Phi, \quad (2)$$

where  $\Omega^+$  is a simple annihilation operator  $a_i$  for an orbital  $\varphi_i$  occupied in  $\Phi$  for the case of ionization, or a spin-adapted orbital replacement operator  $E_i^A$  in the case of excitation (see §5 for the definition of  $E_i^A$ ).

We search for a unitary wave operator

$$W = e^\sigma, \quad \sigma = -\sigma^+ \quad (3)$$

with the property that it transforms  $\Phi$  and  $\Phi'$  simultaneously to the respective exact states  $\Psi$  and  $\Psi'$

$$\Psi = e^\sigma \Phi; \quad \Psi' = e^\sigma \Omega^+ \Phi. \quad (4)$$

If we postulate

$$\Omega \Omega^+ \Phi = \Phi, \quad \Omega \Phi = 0 \quad (5)$$

which holds for the model excitation operators mentioned after (2)—we get the following expression for the exact excitation (ionization) energy

$$\begin{aligned} \Delta E &= \langle \Psi' | H | \Psi' \rangle - \langle \Psi | H | \Psi \rangle \\ &= \langle \Phi | \Omega e^{-\sigma} H e^\sigma \Omega^+ | \Phi \rangle - \langle \Phi | \Omega \Omega^+ e^{-\sigma} H e^\sigma | \Phi \rangle \\ &= \langle \Phi | \Omega [e^{-\sigma} H e^\sigma, \Omega^+] | \Phi \rangle = \langle \Phi | [\Omega, [e^{-\sigma} H e^\sigma, \Omega^+]]_{\pm} | \Phi \rangle \\ &= \langle \Phi | [\Omega, [\{H + [H, \sigma] + \frac{1}{2}[[H, \sigma], \sigma] + \dots\}, \Omega^+]]_{\pm} | \Phi \rangle, \end{aligned} \quad (6)$$

where it is convenient to choose the  $-$  sign (commutator) in  $[\cdot]_{\pm}$  for (particle-number conserving) excitations and the  $+$  sign (anticommutator) for ionization.

There is a stationarity principle (see §4) for energy differences. One can hence determine the optimum wave operator  $W$  by requiring that  $\Delta E$  is stationary with respect

to variations of  $W$  (that conserve the unitarity). To exploit this stationarity principle we choose a basis  $\{R\}$  of antihermitean operators ( $R = -R^\dagger$ ) and expand  $\sigma$  in this basis

$$\sigma = \sum_R f_R R \quad (7)$$

and determine the optimum  $f_R$  by the requirement

$$\frac{\partial \Delta E}{\partial f_R} = 0, \text{ all } R. \quad (8)$$

It is convenient to define the following quantities

$$\begin{aligned} \Delta E_0 &= \langle \Phi | [\Omega, [H, \Omega^\dagger]]_\pm | \Phi \rangle \\ A_R &= \langle \Phi | [\Omega, [[H, R], \Omega^\dagger]]_\pm | \Phi \rangle \\ B_{RS} &= \langle \Phi | [\Omega, [[[H, R], S], \Omega^\dagger]]_\pm | \Phi \rangle \\ C_{RST} &= \langle \Phi | [\Omega, [[[[H, R], S], T], \Omega^\dagger]]_\pm | \Phi \rangle \text{ etc.} \end{aligned} \quad (9)$$

Then (6) becomes

$$\Delta E = \Delta E_0 + \sum_R f_R A_R + \frac{1}{2} \sum_{R,S} f_R f_S B_{RS} + \frac{1}{6} \sum_{R,S,T} f_R f_S f_T C_{RST} + \dots \quad (10)$$

and it results from (8) that

$$A_R + \sum_S f_S B_{RS} + \frac{1}{2} \sum_{S,T} f_S f_T C_{RST} + \dots = 0 \quad (11)$$

$$\Delta E_{\text{opt}} = \Delta E_0 + \frac{1}{2} \sum_R f_R A_R + O(f^3). \quad (12)$$

In principle the system (11, 12) is exact. In practice one can get only an approximation to the exact  $\Delta E$ , because (a) one can never choose a complete operator basis  $\{R\}$ , (b) the Hausdorff expansion in (10) or (11) is infinite and one must truncate it after some commutator rank.

The simplest non-trivial approximation consists in (1) limiting  $\{R\}$  to a basis of one-particle and two-particle operators ( $\varphi_i$  and  $\varphi_j$  are supposed to be occupied in  $\Phi$ ,  $\varphi_p$  and  $\varphi_q$  arbitrary)

$$R = \begin{cases} a_p^\dagger a_i - a_i^\dagger a_p \\ a_q^\dagger a_p^\dagger a_j a_i - a_i^\dagger a_j^\dagger a_p a_q \end{cases} \quad (13)$$

or rather spin adapted linear combinations of such operators.

(2) truncating (10) after the bilinear terms. This makes the system (11) linear

$$A_R + \sum_S f_S B_{RS} = 0; \quad \Delta E = \Delta E_0 + \frac{1}{2} \sum_R f_R A_R \quad (14)$$

This linear approach for energy differences is analogous to the CEPA-0 (linear CP-MET or linearized coupled-cluster) approach for the correlation energy of single closed shell states. It is, *grosso modo* (see §3) equivalent to perturbation theory up to third order with infinite summation of all ladder diagrams. The computational effort is

not larger than for perturbation theory to third order, since the same matrix elements have to be evaluated in either case.

The matrix elements (9) involve only commutators of operators. This Lie-algebraic structure implies that in a diagrammatic formulation only ‘connected’ diagrams contribute. Only such  $R$  or  $S$  contribute to  $A_R$  or  $B_{RS}$ , which have at least one particle or hole index in common with  $\Omega^+$ . In the case of ionization from the orbital  $\varphi$ , only the operators represented graphically on figure 3 contribute in the linear theory. These operators can easily be classified as those that account for: (a) relaxation; (b) spin-polarization; (c) change of external correlation; (d) semi-internal correlation.

The terms internal, semiinternal and external correlation have been defined by Silverstone and Sinanoglu (Sinanoglu 1964; Silverstone and Sinanoglu 1966) in their fundamental paper on electron correlation in open-shell states.

In the zeroth-order approximation where  $\Delta E$  is given by  $\Delta E_0$  one gets just the Koopmans energy, i.e.  $\Delta E_0$  is equal to the Hartree-Fock energy of the orbital that one ‘ionizes off’. In performing separate restricted Hartree-Fock calculations for the neutral ground state  $\Phi$  and the ion  $\Phi'$  and taking the difference one accounts in addition to  $\Delta E_0$  for relaxation. In order to take care of spin-polarization as well, at least unrestricted (better spin-projected unrestricted) Hartree-Fock calculations are necessary.

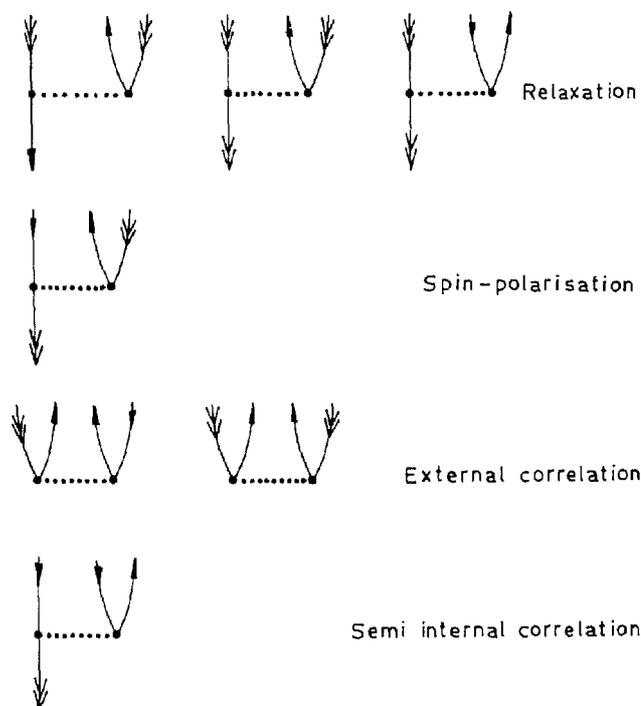


Figure 3. Lowest order contributions to the wave operator for ionization.

Some results are collected in the tables 1 to 4. The general conclusions are:

(a) Except for some special cases [to be discussed under (d)] the results agree well with experiment if the basis sets are large enough.

(b) For ionization from the valence shells, Mulliken's interpretation is confirmed, according to which the approximate validity of Koopmans' theorem is based on a large cancellation of relaxation and change in correlation energy (see tables 1 and 2).

(c) For ionization from inner shells the contribution of relaxation is very strong, while there is only a minor change in correlation energy (Meyer 1971, 1973; Reitz and Kutzelnigg 1979) Koopmans' theorem is hence not a very good approximation. One gets then a much better ionization potential from separate SCF calculations of the

**Table 1.** Ionization potentials for neon (in a.u.), basis: 9s5p2d1f.

	2p	2s
Koopmans-IP	0.84465	1.92392
Relaxation	-0.10687	-0.10668
Spin-polarization	-0.01081	-0.00942
External double substitutions	0.08147	0.04858
Semiinternal double substitutions	-0.01432	-0.07396
Result	0.79413	1.78245
Experiment*	0.7938	1.7813

\* C E Moore 1949 Atomic Energy Levels, Natl. Bur. Stand. (U.S.) Circular 467, Vol. I.

**Table 2.** Ionization potentials for CH<sub>4</sub> (in a.u.), basis 9s1/51.

	1t <sub>2</sub>	2a <sub>1</sub>
Koopmans	0.54430	0.94206
Relaxation	-0.04102	-0.05153
Spin-polarization	-0.00985	-0.00813
External double substitution	0.05556	0.03970
Semiinternal double substitution	-0.01864	-0.08422
Result	0.53036	0.83798
Experiment	0.52920	0.84157

**Table 3.** Ionization potentials for argon (in a.u.), basis 1172.

	3p	3s
Koopmans IP	0.58395	1.27144
Relaxation	-0.04002	-0.05647
Spin-polarization	-0.01092	-0.00662
External double substitution	-0.05730	0.02749
Semiinternal double substitution	-0.01525	-0.28498
Result	0.57507	0.95085
Experiment	0.57920	1.07457

Table 4. Vertical valence shell ionization potentials in eV.

Compound	Ionization potentials			Basis
<u>CH<sub>4</sub></u>				
UNITR*	14.43	22.80		951/51
Experimental	14.40	22.90		
<u>NH<sub>3</sub></u>				
UNITR	10.81	16.63		951/51
Experimental	10.9	15.8 to 16.5		
<u>H<sub>2</sub>O</u>				
UNITR	12.72	14.95	19.09	951/51
Experimental	12.78	14.83	18.72	
<u>HF</u>				
UNITR	16.30	20.12		9521/51
UNITR	16.00	19.99		951/51
Experimental	16.04	19.90		
<u>Ne</u>				
UNITR	21.61	48.50		9521
Experimental	21.60	48.47		
<u>H<sub>2</sub>S</u>				
UNITR	10.25	13.33		1172/51
Experimental	10.47	13.33		
<u>HCl</u>				
UNITR	12.39	16.50		1171/51
UNITR	12.55	16.58		1172/51
Experimental	12.8	16.6		
<u>Ar</u>				
UNITR	15.65	25.87		1172
Experimental	15.76	29.24		
<u>Cl<sup>-</sup></u>				
UNITR	3.68	10.46		1172
Experimental	3.61	?		
<u>N<sub>2</sub></u>				
UNITR	15.02	17.37		952
Experimental	15.60	16.98		

\* the method outlined in §2.

neutral molecule and the ion. This case is not documented here.

(d) In some cases the agreement with experiment is not satisfactory, e.g. for the ionization of a 3s-AO from Ar (see table 3). Here the 'semiinternal' contribution to the IP is unusually large. This is an indication of near-degeneracy of the ionized configuration  $1s^2 2s^2 2p^6 3s 3p^6$  with the 'semiinternally' excited ionic configuration  $1s^2 2s^2 2p^6 3s^2 3p^4 3d$  (it is, with respect to the former configuration, doubly excited  $3p^2 \rightarrow 3s 3d$ ,  $3p \rightarrow 3s$  is 'internal',  $3p \rightarrow 3d$  'external').

Another case of poor agreement between theory and experiment is the ionization potential of  $F^-$  (equivalent to the electron affinity of  $F$ ). Here one finds an unusually large relaxation contribution. If one particular contribution is very large, one can conclude that the lowest order approach (14) is not good enough.

The following remark is in order. Many ionic states are not really bound states, especially those where an electron is ionized from an inner orbital. There is no guarantee that variational calculations converge to such states. The corresponding

Koopmans states are, however, well defined. It also seems that 'direct' methods with the Koopmans energy as starting approximation have no convergence problems.

### 3. Possible improvement of the method of §2

The method proposed by Reitz and Kutzelnigg (1979) leads to rather simple expressions, and does not, in fact, involve more labour than perturbation theory up to 3rd order. It is not entirely true that this method contains all contributions of 3rd order of  $\epsilon$ . In truncating the energy expansion (10) after the bilinear terms one neglects the contribution

$$\frac{1}{3!} \langle \Phi | [\Omega, [[[[H_0, \sigma], \sigma], \sigma], \Omega^+]]_+ | \Phi \rangle, \quad (15)$$

the leading term of which is of  $O(\lambda^3)$ . It is not too difficult to define an alternative hierarchy of truncation, in which one includes terms with  $H_0$  to one order higher in the Hausdorff expansion than terms with  $V$ . It appears, however, that terms like (15) are relatively unimportant.

If one goes to higher orders in the Hausdorff expansion (10) one is led to non-linear systems of equations and the matrix elements become rather complicated. This does not really pay, unless one also increases the particle rank of the basis operators. One can again argue in terms of perturbation theory. To 3rd order in  $\epsilon$  only two-particle operators contribute, while one needs three-particle operators to get all terms of 4th and 5th order in  $\epsilon$ . So the next consistent step in a hierarchy of equations would be to

- (a) truncate the basis after three-particle operators
- (b) truncate the Hausdorff expansion after the term

$$\frac{1}{4!} \langle \Phi | [\Omega, [[[[[H, \sigma], \sigma], \sigma], \Omega^+]]_+ | \Phi \rangle \quad (16)$$

or

$$\frac{1}{4!} \langle \Phi | [\Omega, [[[[[V, \sigma], \sigma], \sigma], \Omega^+]]_+ | \Phi \rangle \quad (17a)$$

and

$$\frac{1}{5!} \langle \Phi | [\Omega, [[[[[[H_0, \sigma], \sigma], \sigma], \sigma], \Omega^+]]_+ | \Phi \rangle. \quad (17b)$$

One can also argue that 3-particle operators are  $O(\lambda^2)$  such that one can reduce the maximum order in the Hausdorff expansion by one for each 3-particle operator.

Although one can thus define a hierarchy that leads eventually to the exact result, this may not be the optimum way. As in the theory of electron correlation of single electronic states, it is recommended that a distinction be made between so-called dynamic and non-dynamic correlation effects (Sinanoglu 1964). In the language of perturbation theory, dynamic correlation effects (which come mainly from the short range Coulomb repulsion) are associated with large energy denominators  $\epsilon$  and hence, small coefficients  $c$

$$c = A/\epsilon; \quad \Delta E = A^2/\epsilon = Ac. \quad (18)$$

Non-dynamic correlation effects result from near degeneracies and are associated with small  $\epsilon$  (in absolute value) and hence, large coefficients  $c$ . Perturbation theory converges often sufficiently fast for dynamic correlation, while this is not the case for nondynamic

correlation effects and it is recommended that care be taken of these as accurately as possible. This can be achieved by using quasidegenerate rather than ordinary perturbation theory—or the non-perturbative analogues of these theories.

In practice this means that one does not consider a single reference state but a manifold of quasidegenerate states together, as in the theory of effective Hamiltonians presented in §6. In the theory of energy differences the analogue would be to consider a manifold of quasidegenerate reference energy differences together. In the case of the ionization potentials of Ar, the states  $1s^2 2s^2 2p^6 3s 3p^6$  and  $1s^2 2s^2 2p^6 3s^2 3p^4 3d$  should be considered together. This is certainly more effective than to go to the next step of the hierarchy using brute force.

#### 4. Superoperator theory

A general theory of energy differences (more precisely: of differences of the eigenvalues of one Hamiltonian) can be based on the superoperator (Liouvillean) formalism (Goscinski and Lukman 1970; Jörgensen 1975; Dalgaard and Simons 1977; Manne 1979; Dalgaard 1979; Weiner and Goscinski 1980; Oddershede 1982; Prasad *et al* 1985). Let  $\hat{H}$  be a Hamiltonian, then we define the corresponding superoperator  $\mathbf{H}$  as

$$\mathbf{H}\hat{X} = [\hat{H}, \hat{X}] = \hat{H}\hat{X} - \hat{X}\hat{H} \quad (19)$$

for arbitrary  $\hat{X}$ .  $H$  acts on operators (while  $\hat{H}$  acts on functions). Let

$$\hat{H}\Psi_\mu = E\Psi_\mu; \quad \hat{P}_{\mu\nu} = |\Psi_\mu\rangle\langle\Psi_\nu|, \quad (20)$$

then

$$\mathbf{H}\hat{P}_{\mu\nu} = (E_\mu - E_\nu)\hat{P}_{\mu\nu} = \omega_{\mu\nu}\hat{P}_{\mu\nu}, \quad (21)$$

i.e. the 'excitation operators' (shift operators)  $\hat{P}_{\mu\nu}$  are eigenoperators of  $\mathbf{H}$  to the eigenvalues  $\omega_{\mu\nu} = E_\mu - E_\nu$ .

If one introduces a scalar product and matrix elements in operator space

$$\langle\hat{A}|\hat{B}\rangle = \text{Tr}\{\hat{A}^+\hat{B}\}; \quad \langle\hat{A}|\mathbf{H}|\hat{B}\rangle = \text{Tr}(\hat{A}^+(H\hat{B})) \quad (22)$$

a stationarity principle for energy differences can be formulated

$$\delta\{\langle\hat{X}|\mathbf{H}|\hat{X}\rangle - \lambda\langle\hat{X}|\hat{X}\rangle\} = 0 \quad (23)$$

One can then expand  $\hat{X}$  in an operator basis, evaluate the matrix elements of  $H$  in this operator basis and get the transition energies  $\omega$  as well as the corresponding excitation operators  $\hat{P}$  from a matrix eigenvalue problem. Note, however, that (23) is only a stationarity—not an extremum—principle. By making (23) stationary one does hence get neither upper nor lower bounds to the respective energy differences. One is only sure that the error of  $\omega$  is quadratic in the error of  $\hat{P}$ .

Usually this expansion method does not present any advantage as compared to the corresponding expansion method for the original Schrödinger equation (20) because an operator basis is always larger than a function basis. The superoperator formalism only becomes competitive if one applies it in Fock space (with the particle number not fixed) rather than in a fixed-particle number Hilbert space. In fact superoperator theory can be applied to ionization only if one interprets  $\hat{H}$  as a Fock space operator. The main advantage of Fock space theory is that the operator basis is much simpler than in fixed particle number Hilbert space (see §7).

### 5. Quantum chemistry in Fock space

The formalism (Kutzelnigg 1981, 1982, 1984a, b; Kutzelnigg and Koch 1983) outlined in this section is essentially equivalent to traditional 2nd quantization, it mainly uses a more compact notation, in particular for particle-number conserving normal products of creation ( $a_p^\dagger = a^p$ ) and annihilation operators ( $a_p$ )—that are defined with respect to an orthonormal one-particle (spin-orbital) basis  $\Psi_p$ . We define

$$\begin{aligned} a_q^p &= a^p a_q = a_p^\dagger a_q \\ a_{rs}^{pq} &= a^p a^q a_s a_r, \text{ etc.} \end{aligned} \quad (24)$$

as well as the corresponding operators summed over spin (which are hence spin-independent, i.e. spin-conserving)

$$\begin{aligned} E_Q^P &= a_{Q\alpha}^{P\alpha} + a_{Q\beta}^{P\beta} \\ E_{RS}^{PQ} &= a_{R\alpha S\alpha}^{P\alpha Q\alpha} + a_{R\alpha S\beta}^{P\alpha Q\beta} + a_{R\beta S\alpha}^{P\beta Q\alpha} + a_{R\beta S\beta}^{P\beta Q\beta} \text{ etc.} \end{aligned} \quad (25)$$

Capital letters always refer to spinfree orbitals, lower case are letters to spin orbitals.

A tensorial notation is also used for matrix elements (bras: lower indices, kets: upper indices)

$$\begin{aligned} \langle \varphi_p | \hat{h} | \varphi_q \rangle &= h_p^q \\ \langle \varphi_p(1) \varphi_q(2) | \frac{1}{r_{12}} | \varphi_r(1) \varphi_s(2) \rangle &= V_{pq}^{rs} \end{aligned} \quad (26)$$

A spinfree Hamiltonian looks then like

$$H = h_Q^P E_P^Q + \frac{1}{2} V_{RS}^{PQ} E_{PQ}^{RS} \quad (27)$$

where the Einstein summation convention is implied.

In practice one has to use a *finite* basis  $\{\varphi_R\}$  of  $M$  (spinfree) orbitals. The  $H$  according to (27) in such a finite basis is invariant under the unitary group  $U(M)$  of all unitarity transformations among the  $M$  basis functions. As a consequence the eigenfunctions of  $H$  must transform as irreducible representations ( $\mathbb{R}$ ) of  $U(M)$ . These  $\mathbb{R}$  are labelled by the particle number  $N$ , the particle statistics (fermions, bosons, spinfree electrons), and the total spin. Basis vectors corresponding to these  $\mathbb{R}$  have been derived by Gelfand and Tsetline (1950), and these have become very popular in quantum chemistry (Hinze 1981). It is also possible to label the  $\mathbb{R}$  by Young diagrams (for electrons with maximally two columns) and the basis vectors by Young tableaux.

All important invariants (except those related to point group symmetry) appear as labels of the  $\mathbb{R}$  of  $U(M)$ .

One should keep in mind that the unitary group  $U(M)$  plays the same natural role in Fock space theory as the symmetric group  $S(N)$  plays in configuration space theory. These two groups have common  $\mathbb{R}$ .

The Fock space analogue to the solution of the Schrödinger equation is the search for a similarity transformation of  $H$  to a 'diagonal' operator  $L$

$$L = W^{-1} H W; \quad L = L_D \quad (28)$$

by means of an operator  $W$ . To make this transformation meaningful one must first define what one understands by 'diagonal'. There are various possibilities (Kutzelnigg

1981, 1982, 1984a, b; Kutzelnigg and Koch 1983), two of which are especially important. In either case one first chooses a one-electron operator  $H_0$  and chooses the orbital basis as eigenfunctions of  $H_0$

$$H_0 = e_p E_p^p \tag{29}$$

Let  $B$  be an arbitrary Fock space operator

$$B = B_0 + B_Q^p E_p^q + \frac{1}{2} B_{RS}^{pq} E_{pq}^{rs} + \dots \tag{30}$$

In the sense of the first definition (universal theory) the ‘diagonal part’  $B_D$  of  $B$  is defined as

$$B_D = B_0 + \delta(e_p, e_q) B_Q^p E_p^q + \delta(e_p + e_q, e_r + e_s) B_{RS}^{pq} E_{pq}^{rs} + \dots \tag{31}$$

with  $\delta(x, y)$  a Kronecker delta. The second definition (theory of effective Hamiltonians) is based on a division of the one-particle space into an ‘active’ subspace (indices  $X, Y, Z \dots$ ) and an ‘inactive’ subspace (indices  $A, B, C \dots$ ). Operators can then be divided into four classes.

- $B$ : closed from below, e.g.  $E_{XY}^{AB}, E_{XY}^{AX}$
- $A$ : closed from above, e.g.  $E_{AB}^{XY}, E_{AX}^{XY}$
- $C$ : closed e.g.  $E_Y^X, E_{ZX}^{XY}$
- $O$ : open e.g.  $E_{AB}^{CD}, E_{AX}^{BY}$ , etc. (32)

The diagonal part of an operator is then defined as

$$B_D = B_C + B_0. \tag{33}$$

For either definition (31) or (33) the ‘nondiagonal’ part  $B_N$  is the complement

$$B_N = B - B_D \tag{34}$$

An operator is called ‘diagonal’ if it is equal to its diagonal part.

We rewrite (28) as

$$HW = WL; \quad L = L_D, \tag{35}$$

and decompose both  $H$  and  $L$  as

$$H = H_0 + \lambda V; \quad L = H_0 + \Delta L, \tag{36}$$

with  $H_0$  given by (29). If  $H_0$  is the bare nuclear Hamiltonian, then

$$V = \frac{1}{2} V_{RS}^{pq} E_{pq}^{rs}. \tag{37}$$

From (35) and (36) we get

$$[H_0, W] = -\lambda VW + W\Delta L. \tag{38}$$

We use the following short hand notation for the formal solution of a commutator equation

$$[H_0, X] = Y \Rightarrow X = -Y_H, \tag{39}$$

where one has to keep in mind that this solution only exists if  $Y_D = 0$ , and that even then the solution  $X$  is not unique, since one can always add to  $X$  any operator  $Z$  which

commutes with  $H_0$ . To make  $B_H$  unique [for  $B$  given by (30)] we define

$$B_H = (e_p - e_q)^{-1} (B_Q^p E_Q^q)_N + (e_p + e_q - e_r - e_s)^{-1} (B_{RS}^{pq} E_{PQ}^{rs})_N + \dots \quad (40)$$

Equation (38) can either be solved by perturbation theory (i.e. expanding  $W$  and  $\Delta L$  in powers of  $\lambda$  and collecting the same powers of  $\lambda$ ) or iteratively (where some convergence acceleration is recommended). Details are found elsewhere (Kutzelnigg 1981, 1982, 1984a, b; Kutzelnigg and Koch 1983).

Equations (35) or (38) do not determine  $W$  and  $L$  uniquely. To make  $W$  and  $L$  unique one has to impose a so-called 'normalization condition'. There are many different possibilities with different merits and drawbacks. The most important ones are the following.

$$\begin{aligned} W_D = 1: & \text{intermediate normalization,} \\ WW^+ = 1; W_D = W_D^+: & \text{canonical unitary normalization,} \\ WW^+ = 1; (\ln W)_D = 0: & \text{separable unitary normalization.} \end{aligned} \quad (41)$$

The third possibility is most conveniently formulated in terms of an operator  $\sigma$

$$W = e^\sigma; \quad \sigma = -\sigma^+ = \sigma_N. \quad (42)$$

The intermediate normalization leads to simpler expressions, but to a non-hermitean  $L$ . If one wants a hermitean  $L$  one must choose  $W$  unitary.

It is finally convenient to introduce a particle-hole formalism (Kutzelnigg 1984a, b), in such a way that normal products of operators are understood in a particle-hole sense but that upper labels are never changed to lower labels and vice versa. If we label holes as  $I, J, K \dots$  and particles as  $A, B, C$  the (particle number and spin conserving) operators are

$$\begin{aligned} \tilde{E}_J^I &= -2\delta_J^I + E_J^I \\ \tilde{E}_B^A &= E_B^A; \tilde{E}_A^I = E_A^I; \tilde{E}_I^A = E_I^A \end{aligned} \quad (43)$$

and respective expressions for operators of higher particle rank. Operators in particle-hole sense are represented by a tilde as  $\tilde{E}_J^I$ .

In evaluating (38) one has to build products of Fock space operators. This can be done by means of a generalized Wick theorem (Kutzelnigg 1981, 1982, 1984a, b; Kutzelnigg and Koch 1983), e.g.

$$\tilde{E}_{CD}^{AB} \tilde{E}_F^E = \tilde{E}_{CDQ}^{ABE} + \delta_C^E \tilde{E}_{FD}^{AB} + \delta_D^E \tilde{E}_{CF}^{AB} \quad (44)$$

Particle indices 'contract' from upper right to lower left, hole lines from lower right to upper left. Contraction over hole lines introduces a factor  $-1$ , 'closed loops' yield a factor  $(-2)$ .

## 6. Effective Hamiltonians and energy differences

Let us choose the definition of  $B_D$  which corresponds to partitioning the one-particle space into 'active' and 'inactive' subspaces and let us also choose the particle-hole-formalism which amounts to discriminating between 'particle' and 'hole' states. This means we can have as many as 4 classes of one-particle states.

(a) active hole states: labels  $F, G \dots$ ,

- (b) inactive hole states: labels  $I, J, K \dots$ ,
- (c) active particle states: labels  $X, Y, Z \dots$ ,
- (d) inactive particle states: labels  $A, B, C$ .

We illustrate this for two examples. Let us first assume that we want to describe the Mg atom both in its neutral ground state (configuration  $1s^2 2s^2 2p^6 3s^2$ ) and in the ground state of the  $\text{Mg}^+$  ion ( $1s^2 2s^2 2p^6 3s$ ). We start with an SCF calculation of the  $\text{Mg}^{2+}$  core ( $1s^2 2s^2 2p^6$ ) and define the AO  $1s, 2s, 2p$ , that are occupied in the core, as inactive hole states. The valence AO  $3s$  will be regarded as an active particle state and all other (virtual) AO as inactive particle states (in this example there are no active hole states).

The effective Hamiltonian is then (it only acts on active orbitals)

$$L = \tilde{L}_\nu + \tilde{L}_X^X \tilde{E}_X^X + \frac{1}{2} \tilde{L}_{XX}^{XX} \tilde{E}_{XX}^{XX}, \quad (45)$$

where  $\tilde{L}_\nu$  is the energy of the 'physical vacuum' (i.e. the  $\text{Mg}^{2+}$  core) and where  $X$  means the  $3s$ -AO. One sees easily that

$$\begin{aligned} E(\text{Mg}^+, 3s) &= \tilde{L}_\nu + \tilde{L}_X^X, \\ E(\text{Mg}, 3s^2) &= \tilde{L}_\nu + 2\tilde{L}_X^X + \tilde{L}_{XX}^{XX}, \\ IP = E(\text{Mg}) - E(\text{Mg}^+) &= \tilde{L}_X^X + \tilde{L}_{XX}^{XX}. \end{aligned} \quad (46)$$

For this particular example we calculate (Koch 1984)

$$\begin{aligned} \tilde{L}_X^X &= -14.945 \text{ eV}, \\ \tilde{L}_{XX}^{XX} &= 7.324 \text{ eV}, \\ IP &= 7.621 \text{ eV (experimental 7.646 eV)}. \end{aligned}$$

The ionization potential (IP) of neutral magnesium is hence easily expressed through the matrix elements of the effective Hamiltonian (45).

An alternative would be to take the ground state of neutral Mg ( $1s^2 2s^2 2p^6 3s^2$ ) as 'physical vacuum' and to start with an SCF calculation of this state. We have then to classify  $1s, 2s$  and  $2p$  as inactive hole states and  $3s$  as an active hole state; all other (virtual) AO are inactive particle states.

The effective Hamiltonian is then

$$L = \tilde{L}_\nu + \tilde{L}_F^F \tilde{E}_F^F + \frac{1}{2} \tilde{L}_{FF}^{FF} \tilde{E}_{FF}^{FF}, \quad (47)$$

where  $\tilde{L}_\nu$  is now the energy of the Mg ground state. The IP of Mg (for ionization for the  $3s$ -AO) is then directly  $-\tilde{L}_F^F$ .

It is not easy to say *a priori* which of the two choices is better. One may, in view of the  $3s/3p$  near-degeneracy also want to consider the  $3p$ -AO as active particles, which makes the effective Hamiltonian more complicated, but may make the constructions of its elements easier.

For the case of the '3s-IP' of Ar we have to regard  $1s, 2s$  and  $2p$  as inactive hole states,  $3s$  and  $3p$  as active hole states and  $3d$  as active particle states—or alternatively  $3s, 3p$  and  $3d$  as active particle states. In either case the IP is not directly expressible through the matrix elements of the effective Hamiltonian, but a secular problem in the active space has to be performed first.

Effective Hamiltonians like those presented (Kutzelnigg 1984a, b; Kutzelnigg and Koch 1983) have—in a different notation—also been used by other authors (Bloch 1958; Morita 1963; Brandow 1967; Kirtman 1968; Amat *et al* 1971; Schucan and Weidenmüller 1973; Klein 1974; Lindgren 1974; Jørgensen 1975; Kvasnicka 1977; Barret 1977; Shavitt and Redmon 1980; Soliverz 1981; Sun *et al* 1981; Powers and Zuker 1981; Durand 1983).

### 7. The Fock space Liouville operator

Let  $\hat{H}$  be a Fock space Hamiltonian as given by (27). We define (in analogy to §4) the Fock space Liouvillean  $\mathbf{H}$  via

$$\mathbf{H}\hat{Y} = [\hat{H}, \hat{Y}]. \quad (48)$$

The eigenstates of  $\mathbf{H}$  according to

$$\mathbf{H}\hat{X} = \omega\hat{X} \quad (49)$$

are now transitions between eigenstates of  $\hat{H}$  either for the same or different numbers of particles. In analogy to the particle number operator  $\hat{N}$  there is the superoperator  $\mathbf{N}$  of the change of the number of particles

$$\mathbf{N}\hat{Y} = [\hat{N}, \hat{Y}]. \quad (50)$$

The eigenoperators of  $\mathbf{H}$  are, of course, also eigenoperators of  $\mathbf{N}$ . Let  $\hat{H}_0$  be a one-particle operator

$$\hat{H}_0 = e_p E_p^p, \quad (51)$$

then every  $E_S^R$  is eigenoperator of  $\mathbf{H}_0$  to the eigenvalue  $(e_R - e_S)$  and of  $\mathbf{N}$  to the eigenvalue 0 (no change in the number of particles). The following operators

$$E_{SP}^{RP}, E_{PS}^{RP}, E_{SPQ}^{RPQ}, \text{ etc.} \quad (52)$$

are also eigenoperators of  $\mathbf{H}_0$  and  $\mathbf{N}$  to the same eigenvalues. Any eigenvalue of  $\mathbf{H}_0$  is hence highly degenerate ( $E_S^R$  means 'unconditional' excitation from  $\varphi_S$  to  $\varphi_R$ , while  $E_{SP}^{RP}$  means excitation from  $\varphi_S$  to  $\varphi_R$  provided that  $\varphi_P$  is occupied etc.). This degeneracy is to a large extent removed by the interaction superoperator  $\mathbf{V}$ . It is obvious that degenerate or quasidegenerate perturbation theory has to be applied, unless one succeeds in removing this degeneracy by referring to super operators that commute with  $\mathbf{H}$ .

If one performs perturbation theory for energy differences with the Fock space Liouvillean formalism one gets the same results as from perturbation theory of the two states separately and forming the difference. However, due to the Lie algebraic structure of the theory, contributions that are not connected to the excitation (or ionization) and that cancel in the difference do not appear at the outset. This leads to a simplification.

The generalization of the Frobenius trace metric to Fock space operators is non-trivial but possible (Kutzelnigg 1986).

A non-perturbative approach to ionization potentials leads to the Reitz-Kutzelnigg method of §2 as the simplest non-trivial approximation. For excitation energies one is easily lead to RPA (random phase approximation) as a possible first step in a hierarchy of approximations. Alternative hierarchies have been proposed by Schirmer *et al* (1983).

As for any operator or superoperator the resolvent  $\mathbf{G}(z)$  of the Fockspace Liouvillean  $\mathbf{H}$  can be defined via

$$\mathbf{G}(z) (z - \mathbf{H}) = \mathbf{1}, \quad (53)$$

which means explicitly

$$\mathbf{G}(z) (z \hat{Y} - [\hat{H}, \hat{Y}]) = \hat{Y} \quad (54)$$

for all  $\hat{Y}$  in the domain of  $\mathbf{H}$ . One also writes formally

$$\mathbf{G}(z) = (z - \mathbf{H})^{-1}. \quad (55)$$

We also define the unperturbed resolvent  $\mathbf{G}_0$ , related to the  $\hat{H}_0$  given by (51)

$$\mathbf{G}_0(z) = (z - \mathbf{H}_0)^{-1}. \quad (56)$$

All normal products of an arbitrary number of creation and annihilation operators for the eigenstates of  $\hat{H}_0$  are eigenoperators of  $\mathbf{G}_0(z)$ , e.g.

$$\begin{aligned} \mathbf{G}_0(z) a_p &= (z + e_p)^{-1} a_p \\ \mathbf{G}_0(z) a^q &= (z - e_q)^{-1} a^q \\ \mathbf{G}_0(z) a_{rs}^{pq} &= (z - e_p - e_q + e_r + e_s)^{-1} a_{rs}^{pq} \end{aligned} \quad (57)$$

The well-known relation between  $G(z)$ ,  $G_0(z)$  and  $V$  also holds in this case\*

$$\mathbf{G}(z) = \mathbf{G}_0(z) + \mathbf{G}_0(z) \mathbf{V} \mathbf{G}(z). \quad (58)$$

The resolvent  $\mathbf{G}(z)$  has poles for all those values of  $z$  that are equal to the eigenvalues of  $\mathbf{H}$  i.e. to differences of eigenvalues of  $\hat{H}$ . This is usually too much information. One wants to filter it to transitions from a given state  $\Psi$  to, say all the states in which the particle number is reduced by 1—i.e. to ionization. This can be achieved by considering the expectation value

$$\langle \Psi | [\Omega, \{ \mathbf{G}(z) \Omega^+ \}]_+ | \Psi \rangle, \quad (59)$$

where

$$\Omega^+ = a_i, \quad (60)$$

is a model ionization operator and  $\Psi$  the exact wave function of the ground state. From (59) there is a straightforward way to the theory of Green's functions for reduced particle number or of propagators and to a time-independent theory of these Green's functions (Kutzelnigg 1986) which are conventionally introduced and evaluated in a time-dependent formulation (see for example, Kirshnitz 1967; Fetter and Walecka 1971; Parry 1973), and which have largely been used for the direct calculation of energies by various authors, primarily by Cederbaum and his group (Cederbaum 1973; Cederbaum and Domcke 1977). Time-independent approaches to Greens functions have also been considered by other authors (Goscinski and Lukman 1970; Jörgensen 1975; Dalgaard and Simons 1977; Dalgaard 1979; Manne 1979; Weiner and Goscinski 1980; Oddershede 1982; Prasad *et al* 1985).

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\* This is sometimes called a 'Lippman-Schwinger' equation, although the latter refers to a different physical situation, viz. the inclusion of scattering boundary conditions.

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