

## ON RAYLEIGH-SCHRÖDINGER AND GREEN'S-FUNCTION CALCULATIONS OF IONIZATION POTENTIALS AND ELECTRON AFFINITIES

A.J. HERNÁNDEZ\*

*Department of Chemistry, Indiana University, Bloomington, Indiana 47401, USA*

and

P.W. LANGHOFF\*\*

*Department of Chemistry, Indiana University, Bloomington, Indiana 47401, USA  
and Joint Institute for Laboratory Astrophysics, National Bureau of Standards and University of Colorado,  
Boulder, Colorado 80309, USA*

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Connections between first-quantized Rayleigh-Schrödinger perturbation-theory and one-particle Green's-function calculations of the ionization potentials and electron affinities of atoms and molecules are reported.

### 1. Introduction

The ionization potentials and electron affinities of atoms and molecules can be obtained from the differences of appropriately calculated neutral and ionic energies [1-8], and from the poles of one-particle Green's functions [9-25] constructed employing various approximations to the self-energy [26-35]. Although these two procedures are apparently different in spirit and outward appearance, recent calculations [6,14] indicate that identical numerical results can be obtained from them in certain cases under appropriate conditions. A clarifying theoretical investigation of interconnections between energy-difference and Green's-function calculations of ionization potentials and electron affinities in atoms and molecules would be helpful.

In the present letter, connections between energy-difference and Green's-function calculations of ionization potentials using perturbation theory are reported for closed-shell systems, based on a detailed analysis

[36] of both approaches employing various diagrammatic techniques [37-41]. The equivalence of energy-difference ionization-potential calculations employing Rayleigh-Schrödinger perturbation theory in a canonical Fock basis of the  $N$ -electron system with the so-called quasi-particle Green's-function approximation [42] is proved to third order, and shown to fail in the fourth- and higher-orders of perturbation theory. These results follow most directly from the irreducible nature of the self-energy and a second- and third-order isomorphism between ionization-potential and self-energy diagrams when a Fock basis is employed [40,41]. Illustrative calculations on two- and four-electron systems indicate that the effects of iteration in the solution of the Schwinger-Dyson equation on the locations of ionization-potential poles are generally small when the self-energy is evaluated to second or third order. The possibility of obtaining conjugate pairs of complex poles from the Green's function formalism when the self-energy is evaluated in third order is indicated. It is noted that neither energy-difference nor Green's-function calculations in perturbation theory employing  $L^2$  functions converge for the ionization potentials of core states which are unstable to Auger effect [43].

\* CONICIT Venezuelan Fellow.

\*\* JILA Visiting Fellow, 1976.

The theoretical development is given in section 2, illustrative calculations in the cases of the two- and four-electron isoelectronic series are given in section 3, and concluding remarks are made in section 4.

## 2. Theory

The customary Rayleigh–Schrödinger series for the ground-state energy of an  $N$ -electron system employing the Hartree–Fock approximation in zeroth order can be written in the form [44,45],

$$E(N) = E^{(0)}(N) + E^{(1)}(N) + E^{(2)}(N) + \dots, \quad (1)$$

where  $E^{(0)}(N) + E^{(1)}(N)$  is the Hartree–Fock energy, and the higher-order terms  $E^{(n)}(N)$  provide a series representation of the correlation energy. A useful approximation to the ionization potential associated with the removal of the  $k$ th canonical spin orbital ( $1 \leq k \leq N$ ) is given by the difference

$$\Delta E_k = E_k(N-1) - E(N), \quad (2)$$

where

$$E_k(N-1) = E_k^{(0)}(N-1) + E_k^{(1)}(N-1) + E_k^{(2)}(N-1) + \dots \quad (3)$$

is the corresponding Rayleigh–Schrödinger series for the  $(N-1)$ -electron system, obtained employing a Hartree–Fock function in zeroth order comprised of  $N-1$  canonical Fock spin orbitals from the  $N$ -electron system. In this case the ionization potential can be written

$$\Delta E_k = \Delta E_k^{(0)} + \Delta E_k^{(1)} + \Delta E_k^{(2)} + \dots, \quad (4)$$

where

$$\Delta E_k^{(0)} + \Delta E_k^{(1)} = -\epsilon_k \quad (5)$$

corresponds to the Koopmans approximation [46], and the higher-order terms  $\Delta E_k^{(n)}$  provide a series for relaxation effects and the change in correlation energy upon the removal of the  $k$ th canonical spin orbital. The perturbation-theory corrections to the Koopmans approximation can be calculated from the conventional expressions [45] employing as a basis the appropriate complementing complement to the occupied canonical Fock orbitals.

An alternative expression for the ionization potential

associated with the removal of the  $k$ th canonical spin orbital is obtained from the  $k$ th pole in the left-hand plane of the one-particle Green's function [47–52]

$$G(z) = [zI - h - \Sigma(z)]^{-1}, \quad (6)$$

where the Fock matrix  $h$  and self-energy matrix  $\Sigma(z)$  are constructed in the occupied and virtual Fock basis of the  $N$ -electron system. Since the shifts of the ionization potentials from their Koopmans values [eq. (5)], – the so-called Koopmans defects – are relatively small the poles  $\omega_k^-$  of  $G(z)$  are conveniently obtained from iterative solution on the real axis of the eigenvalue problem

$$\det|h + \Sigma(\epsilon) - I\epsilon| = 0, \quad (7)$$

starting from the so-called quasi-particle value  $\Sigma(\epsilon_k)$  of the self-energy matrix [42]. Although various approximations to the latter are useful [26–35], a systematic approach is provided by the perturbation series [37–42]

$$\Sigma(z) = \Sigma^{(2)}(z) + \Sigma^{(3)}(z) + \dots, \quad (8)$$

where the first-order term vanishes identically as a consequence of the use of Fock spin orbitals in zeroth order.

In order to establish connections between the energy difference and Green's-function approaches to ionization potentials, it is convenient to evaluate the terms in eq. (4) algebraically, and to compare these explicitly with results obtained from eqs. (7) and (8). Although the lowest-order terms in the developments of eqs. (1) to (5) and (6) to (8) can be constructed algebraically with relative ease, the higher-order terms are difficult to evaluate explicitly. Diagrammatic techniques are particularly useful in this connection [37–42]. The terms in the Rayleigh–Schrödinger series of eqs. (1), (3), and (4) are conveniently determined employing operators in normal form and appropriate distinct Hugenholtz diagrams [40,41], with subsequent vertex expansion to obtain the corresponding Goldstone energy diagram in each order [39]. In this way explicit energy-difference expressions involving integrals over Fock orbitals are obtained. As an alternative to this approach, modified Brandow rules [38] are employed in the construction of energy expressions corresponding to Hugenholtz diagrams, providing results in terms of integrals over Fock spin orbitals, which are then reduced by appropriate spin summations. The necessary self-

energy expressions are obtained employing the appropriate essentially distinct Hugenholtz diagrams [28,40,41], followed by subsequent vertex expansion to obtain the complete algebraic expressions.

Inspection of the expressions obtained from the detailed diagrammatic analysis shows that [36]

$$\Delta E_k^{(0)} + \Delta E_k^{(1)} = -\epsilon_k, \quad (9a)$$

$$\Delta E_k^{(2)} = -\Sigma_{kk}^{(2)}(\epsilon_k), \quad (9b)$$

$$\Delta E_k^{(3)} = -\Sigma_{kk}^{(3)}(\epsilon_k), \quad (9c)$$

$$\Delta E_k^{(n)} \neq -\Sigma_{kk}^{(n)}(\epsilon_k), \quad n \geq 4. \quad (9d)$$

Here, eq. (9a) corresponds to the Koopmans result [eq. (5)], eq. (9b) confirms the previously established [29] equivalence of the second-order Rayleigh–Schrödinger correction with the second-order quasi-particle approximation [42], eq. (9c) extends this result to the third order, and eq. (9d) indicates that the equivalence of Rayleigh–Schrödinger perturbation theory for the correction to the Koopmans result with the quasi-particle approximation fails in the fourth and higher orders. Although eqs. (9a) and (9b) can be obtained using the conventional first-quantized approach based on Slater determinants in the evaluation of the Rayleigh–Schrödinger terms, the diagrammatic analysis is particularly helpful in establishing eqs. (9c) and (9d). It is appropriate to note that eqs. (9b) and (9c) can also be regarded as a consequence of an isomorphism between ionization-potential [40,41] and self-energy [28] diagrams of the Hugenholtz type in second and third order. Moreover eq. (9d) follows from the fact that the self-energy appearing in eqs. (6) to (8) corresponds to irreducible diagrammatic contributions only [39], whereas the diagrammatic representation of the Rayleigh–Schrödinger series [eqs. (1), (3), and (4)] includes reducible contributions in fourth and higher order [40,41]. Indeed, when a zeroth-order approximation other than the Hartree–Fock approach is employed, reducible contributions appear in the Rayleigh–Schrödinger ionization-potential series in second and higher order, non-zero first-order terms are present in the self-energy series, and eqs. (9b) and (9c) fail in this case. Although the third-order self-energy contributions have been described and employed in previous calculations [10,14,28,30,32,34], the explicit algebraic expressions have apparently not appear-

ed in the literature. They can be constructed most simply [36] from the self-energy parts of third-order excitation diagrams [40,41].

Eqs. (9) clarify the observed similarities between ionization potentials obtained from the Rayleigh–Schrödinger development [6] and from the Green’s-function formalism [14]. Specifically, it is evident from eqs. (9a), (9b), and (9c) that the Rayleigh–Schrödinger and Green’s-function values differ in second and third order only by the effects of iteration in the solution of eq. (7) when the quasi-particle approximation is used as the starting value for the self-energy [eq. (8)]. In order to determine the magnitude of these effects, it is helpful to perform some illustrative calculations on appropriately chosen systems.

### 3. Calculations

Calculations of the ionization potentials of two- and four-electron atoms and ions employing the Rayleigh–Schrödinger and Green’s-function methods described in the preceding section are reported here. Basis sets of good quality are available in each case for these systems for the construction of occupied and virtual Fock orbitals [53]. Consequently, it is anticipated that adequate convergence can be achieved in calculations of the separate contributions to ionization potentials, and that conclusions drawn on basis of these values will not be strongly basis-set dependent. By contrast, although the ionization potentials of larger systems are of interest, inadequate basis sets can render unreliable a comparison of Rayleigh–Schrödinger and Green’s-function calculations in these cases.

Basis sets of 5s, 4p, 3d Slater-type orbitals [53] are used in the calculations on the two-electron systems. Conventional Rayleigh–Schrödinger perturbation-theory energy calculations to third order indicate that the basis sets provide approximately 95% of the correlation energy in all cases. In table 1 are shown the ionization potentials obtained from the Koopmans approximation, from the Rayleigh–Schrödinger or quasi-particle approximation in second and third order, and from the fully-iterated solution of the Dyson equation [eq. (7)] employing the self-energy to second and third order\*.

\*For footnote see next page.

Table 1  
Ionization potentials in the two-electron isoelectronic series (atomic units)

| Atom             | Orbital | SCF<br>$-\epsilon_k$ | Quasi-particle <sup>a)</sup> |                       | Dyson-equation <sup>b)</sup> |                       | Exact <sup>c)</sup> |
|------------------|---------|----------------------|------------------------------|-----------------------|------------------------------|-----------------------|---------------------|
|                  |         |                      | $\Sigma(2)$                  | $\Sigma(2)+\Sigma(3)$ | $\Sigma(2)$                  | $\Sigma(2)+\Sigma(3)$ |                     |
| H <sup>-</sup>   | 1s      | 0.0470               | 0.0257                       | 0.0271                | 0.0292                       | 0.0275                | 0.0277              |
| He               | 1s      | 0.9180               | 0.9055                       | 0.9027                | 0.9060                       | 0.9035                | 0.9036              |
| Li <sup>1+</sup> | 1s      | 2.7926               | 2.7868                       | 2.7790                | 2.7810                       | 2.7793                | 2.7800              |
| Be <sup>2+</sup> | 1s      | 5.6673               | 5.6563                       | 5.6549                | 5.6564                       | 5.6551                | 5.6556              |
| B <sup>3+</sup>  | 1s      | 9.5422               | 9.5310                       | 9.5300                | 9.5311                       | 9.5301                | 9.5311              |
| C <sup>4+</sup>  | 1s      | 14.4168              | 14.4062                      | 14.4054               | 14.4063                      | 14.4055               | 14.4065             |
| N <sup>5+</sup>  | 1s      | 20.2926              | 20.2819                      | 20.2812               | 20.2819                      | 20.2813               | 20.2820             |
| O <sup>6+</sup>  | 1s      | 27.1668              | 27.1566                      | 27.1560               | 27.1568                      | 27.1561               | 27.1576             |

a) Values corresponding to Rayleigh–Schrödinger perturbation theory [eq. (4)].

b) Fully-iterated solution of the Dyson equation [eq. (7)].

c) Nonrelativistic values calculated by Pekeris [54].

Evidently, the Koopmans values provide excellent first approximations to the available precise calculations [54] in each case except the negative hydrogen ion. The Rayleigh–Schrödinger series and Dyson-equation solutions provide improved ionization potentials in each of the two orders considered for the systems H<sup>-</sup> to Be<sup>2+</sup>, and the third-order results are in excellent accord with the exact values in these cases. For the systems B<sup>3+</sup> to O<sup>6+</sup> the Dyson-equation and Rayleigh–Schrödinger results provide improved potentials in second order, but the third-order results fall below the exact values. Evidently, both sets of third-order results underestimate the ionization potentials in all cases, although the discrepancies are quite small. The calculated third-order Koopmans defects are all within 5% of the exact values, and hence in accord with the observation that the basis sets employed provide 95% of the correlation energy in third-order perturbation theory. Moreover, the Dyson-equation values are evidently in good agreement with the

corresponding Rayleigh–Schrödinger or quasi-particle results in each order in every case, indicating that the effects of iteration of eq. (7) are very small in these cases.

Basis sets of 6s, 5p, 2d Slater-type orbitals [53] are used in the study of the four-electron systems. Third-order Rayleigh–Schrödinger calculations in these cases provide approximately 85% of the total correlation energies. In table 2 the ionization potentials obtained are compared with corresponding experimental values [8]. The Koopmans values evidently provide useful first approximations to both the 1s and 2s ionization potentials in every case except possibly Li<sup>-</sup>. In the cases of the 2s ionization potentials both the Rayleigh–Schrödinger and Dyson-equation results for the four-electron systems provide improved values in each order and the effects of iteration are apparently small in each order. Moreover, the calculated third-order Koopmans defects account for approximately 75% of the experimental values, except in the case of Li<sup>-</sup>. Both sets of results for the 1s ionization potentials give no indication of convergence, however. This is in accord with the observation that core states of the type (1s2s<sup>2</sup>)<sup>2</sup>S are unstable with respect to Auger effect [43]. Consequently, the appropriate level shifts from the Hartree–Fock values must be calculated by mixing in the degenerate (1s<sup>2</sup>ks)<sup>2</sup>S continuum states according to the prescriptions of Feshbach–Fano theory [55,56]. Conventional L<sup>2</sup> basis set calculations of the shifts in perturbation theory are not expected to converge in these cases.

\* The poles of the Green's function need not necessarily lie on the real axis when the self-energy is evaluated in third and higher orders [42]. In the present studies, the 1s and 2s ionization-potential poles obtained in third order are all real, although conjugate pairs of complex poles corresponding to high-lying ionic states associated with combined ionization and core excitation are generally found in the far left-hand plane. Moreover additional studies [36] not reported here indicate that the pole associated with the removal of a 2s orbital in Ar apparently shifts off the real axis when the third-order self-energy correction is introduced.

Table 2  
Ionization potentials in the four-electron isoelectronic series (atomic units)

| Atom            | Orbital | SCF<br>$-\epsilon_k$ | Quasi-particle <sup>a)</sup> |                             | Dyson-equation <sup>b)</sup> |                             | Exptl. <sup>c)</sup> |
|-----------------|---------|----------------------|------------------------------|-----------------------------|------------------------------|-----------------------------|----------------------|
|                 |         |                      | $\Sigma^{(2)}$               | $\Sigma^{(2)+\Sigma^{(3)}}$ | $\Sigma^{(2)}$               | $\Sigma^{(2)+\Sigma^{(3)}}$ |                      |
| Li <sup>-</sup> | 1s      | 2.3223               | 2.1469                       | 2.1036                      | 2.2102                       | 2.1859                      | 2.0                  |
| Li <sup>-</sup> | 2s      | 0.0142               | 0.0179                       | 0.0189                      | 0.0176                       | 0.0185                      | 0.0226               |
| Be              | 1s      | 4.7309               | 4.5917                       | 4.5551                      | 4.6118                       | 4.5874                      | 4.45                 |
| Be              | 2s      | 0.3084               | 0.3280                       | 0.3347                      | 0.3274                       | 0.3334                      | 0.3426               |
| B <sup>+</sup>  | 1s      | 8.1843               | 8.0528                       | 8.0223                      | 8.0630                       | 8.0388                      | 7.2                  |
| B <sup>+</sup>  | 2s      | 0.8732               | 0.9030                       | 0.9136                      | 0.9023                       | 0.9122                      | 0.9245               |
| C <sup>2+</sup> | 1s      | 12.6491              | 12.5194                      | 12.4945                     | 12.5260                      | 12.5041                     | 11.3                 |
| C <sup>2+</sup> | 2s      | 1.6935               | 1.7308                       | 1.7450                      | 1.7301                       | 1.7433                      | 1.7599               |
| N <sup>3+</sup> | 1s      | 18.1200              | 17.9886                      | 17.9665                     | 17.9937                      | 17.9733                     | 16.5                 |
| N <sup>3+</sup> | 2s      | 2.7667               | 2.8111                       | 2.8228                      | 2.8103                       | 2.8264                      | 2.8472               |
| O <sup>4+</sup> | 1s      | 24.5922              | 24.4606                      | 24.4405                     | 24.4645                      | 24.4455                     | 22.4                 |
| O <sup>4+</sup> | 2s      | 4.0907               | 4.1417                       | 4.1623                      | 4.1408                       | 4.1602                      | 4.1859               |

a) Values corresponding to Rayleigh–Schrödinger perturbation theory [eq. (4)].

b) Fully-iterated solution of the Dyson equation [eq. (7)].

c) Experimental values taken from the tabulation of Day et al. [8].

#### 4. Concluding remarks

Connections between Rayleigh–Schrödinger and Green's-function calculations of ionization potentials in closed-shell systems are reported, based on a diagrammatic analysis of the appropriate expressions in each case. The equivalence of the Green's-function approach in the so-called quasi-particle approximation with conventional Rayleigh–Schrödinger perturbation theory is demonstrated to third order in the self-energy, and shown to fail in fourth and higher orders of perturbation theory when a Fock basis is employed. These results follow most directly from a previously unidentified isomorphism between ionization-potential and self-energy diagrams in second and third order. The failure of the theorem in fourth and higher orders can be attributed to the irreducible nature of the self-energy operator, and to the presence of terms of a reducible nature in fourth and higher order in the conventional Rayleigh–Schrödinger perturbation series. Calculations of the ionization potentials of two- and four-electron systems indicate that the effects of iteration in the solution of the Dyson equation are generally small in second and third order. The failure to converge of  $L^2$  perturbation theory calculations for the ionization potentials of core electrons is attributed to their Auger instability, necessitating a Fano–Feshbach treatment.

Additional related comments are given elsewhere [36].

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