Quasi-Particle Equation from the Configuration-Interaction (CI) Wave-Function Method

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Abstract

The Green-function method is a well-known way to reduce the quantum mechanical problem of n electrons moving in the field of clamped nuclei to the problem of solving a one-electron Schrödinger equation (the quasi-particle equation) involving a pseudopotential (the self-energy). This method is widely used in solid-state, low-energy electron-molecule scattering, ionization, and electron attachment theory, and much work has focused on finding accurate self-energy approximations. Unfortunately, the operator nature of the fundamental quantity (Green function) in the usual quasi-particle equation formalism significantly complicates the derivation of self-energy approximations, in turn significantly complicating applications to inelastic scattering and multiconfigurational bound-state problems. For these problems or wherever the operator approach becomes inconvenient, we propose an alternative quasi-particle equation derived wholly within a configuration interaction wave-function formalism and intended to describe the same phenomenology as does the Green function quasi-particle equation. Our derivation refers specifically to electron removal but is readily generalized to electron attachment and scattering. Although the Green function and wave-function quasi-particle equations are different, we emphasize the parallels by rederiving both equations within the equations-of-motion formalism and then producing a wave-function analog of the Green function two-particle-hole Tamm–Dancoff approximation.

1. Introduction

The Green-function method is a well-known way to reduce the quantum mechanical problem of n electrons moving in the field of clamped nuclei to the problem of solving a one-electron Schrödinger equation (the quasi-particle equation) [1] involving a pseudopotential (the self-energy.) This approach has been widely used in problems as diverse as the band structure of solids [2], molecular photoelectron spectra [3], and elastic-scattering of a slow electron with a molecule [4]. The eigenvalues of the quasi-particle equation (QPE) are ionization potentials and electron affinities, whereas the eigenfunctions provide scattering information. One advantage of the QPE is that it is more readily compared with other one-electron equations such as in the Kohn–Sham density functional formalism [5, 6]. However, the primary advantage of the Green function QPE approach is that the most important many-body effects are concentrated in the self-energy, which may then be approximated. Particular Green function approxi-

mations are available from the functional derivative [7], equations-of-motion [8], and diagrammatic Green function [3] formalisms. Approximations are sometimes facilitated by physical interpretations of the self-energy that arise directly from the one-particle picture [9]. Nevertheless, all approaches suffer from difficulties associated with the fact that the important fundamental quantity (the one-electron Green function) is an operator rather than a wave function. These difficulties arise in somewhat different ways for the uninitiated and the expert. The operator formalism significantly complicates Green function derivations [2, 10, 11] and would seem to make the method opaque to many potential users. Even for those who have succeeded in understanding the basic method, the operator formalism still makes it difficult to extract a wave-function interpretation where such an interpretation is desirable (e.g., correlation and relaxation effects during ionization [12]) and even where it is essential (e.g., separation of closed and open channels in low-energy electron-molecule scattering [13, 14]). Furthermore, the introduction of a new (operator) metric leads to the need to calculate new types of matrix elements, often of very complicated types involving high-order reduced density matrices [15] and for which efficient wave-function methods have yet to be adapted [16, 17]. For these reasons, we propose an alternative configuration interaction (CI) wave-function QPE formalism that avoids the aforementioned difficulties of the usual Green function QPE by originating wholly within a wave-function formalism, but that shares many important properties with the Green function QPE.

The spirit of the present work is most closely related to historical developments in the theory of low-energy electron-molecule scattering that were motivated by the success of the phenomenological optical potential theory of scattering [18–20]. The optical potential was soon identified with the Green function self-energy [21]. However, a "generalized optical potential" was derived within the framework of a wave-function formalism [13] at about the same time. This suggests the existence of a wave-function analog of the Green function QPE. The wave-function QPE is further developed in this paper to make it as similar as possible to the Green function QPE without sacrificing the basic advantages of a wave-function formalism.

We will give an explicit answer to the question of the correspondence between our wave-function QPE and the Green function QPE only for the case of ionization, but it will be evident that only minor modifications are necessary to obtain the corresponding scattering equations. *Second-quantized notation is used throughout,* but the required level of sophistication can be obtained from the first chapter of any one of a number of books on many-body theory [10, 11, 22] or later chapters of first-year graduate texts in quantum mechanics (see, e.g., chap. 10 of [23]). Spin orbitals are used throughout, and certain infinitessimals that occur in detailed Green function and scattering theory work have been ignored (i.e., set to zero). Nevertheless, we are sure that the interested reader will be able to supply the missing infinitessimals (if need be) by comparison with appropriate related Green function or scattering theory work.

Commutators and anticommutators will be denoted by

$$[\hat{A}, \hat{B}] \equiv \hat{A}\hat{B} - \hat{B}\hat{A} \qquad (1.1)$$

and

$$\{\hat{A}, \hat{B}\} \equiv \hat{A}\hat{B} + \hat{B}\hat{A}, \tag{1.2}$$

respectively.

The remainder of this paper is organized as follows: We seek a wave-function QPE whose eigenvalues and eigenfunctions agree as closely as possible with the usual Green function QPE. Hence, we begin (in Section 2) with a review of the Green function QPE that also serves to introduce some notation and to review of some of the applications of QPEs. The more difficult aspects of the Green function formalism have been avoided as much as possible, consistent with our objective of deriving a QPE within the conceptually simpler wave-function formalism. Our objective, the CI QPE, is obtained in Section 3 using the Green function QPE as a guide. The remainder of the paper consists in clarifying the relationship between these two QPEs. This is first accomplished in Section 4 by rederiving them both within a single formalism (i.e., using the equations-of-motion method) and is accomplished again at a more practical level in Section 5 by deriving a wave-function analog of the Green function two-particle-hole Tamm–Dancoff approximation. Our conclusions are given in Section 6. Three appendices have also been included where necessary to make the paper self-contained (Appendices A and B) or as a technical aside (Appendix C).

2. Green Function Quasi-Particle Equation

The Green function quasi-particle equation (QPE)

$$[\hat{F} + \hat{\Sigma}^{GF}(\omega)]\chi = \omega\chi \tag{2.1}$$

is a Hartree–Fock-like equation involving the Fock operator $\hat{F}$ and the self-energy $\hat{\Sigma}^{GF}(\omega)$, which will be described in more detail in later sections. The primary objective of the present section is to discuss the QPE eigenvalues and eigenvectors as a prelude to deriving a wave-function QPE in Section 3 with closely related eigenvalues and eigenvectors.

The Green function QPE describes the physics of vertical ionization

$$\begin{array}{ccc} M & \longrightarrow & M^+ & + e^- \\ \Psi_0^{(n)} & & \Psi_I^{(n-1)} \end{array} \tag{2.2}$$

and vertical electron attachment

$$\begin{array}{ccc} M & + e^- \longrightarrow & M^- \\ \Psi_0^{(n)} & & \Psi_I^{(n+1)} \end{array} \tag{2.3}$$

in terms of "particles" and "holes." In particular, the QPE eigenvalues and eigenfunctions are the energies and wave functions for one extra or one less electron. For convenience, we will talk about the "parent neutral," "cation," and "anion" states, although this terminology suggests a prticular application of the general formalism. Superscripts in parentheses indicate particle number. Capital Latin subscripts are indices labeling many-electron states.

Second-quantized notation is convenient for describing the QPE solutions (and for our subsequent manipulations) because the electronic Hamiltonian

$$\hat{H} = \sum_{r,s} h_{r,s} \hat{a}_r^\dagger \hat{a}_s + \frac{1}{4} \sum_{p,q,r,s} v_{pq,rs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s \qquad (2.4)$$

is independent of particle number. The matrices **h** and **v** are constructed in the usual way from one-electron (i.e., kinetic energy and nuclear attraction) and two-electron (i.e., electron repulsion) operators, respectively ($v_{pq,rs} = -v_{pq,sr}$), and $\hat{a}_r$ is the annihilation operator for spin orbital ϕ_r. For simplicity, we will assume that the spin orbitals are orthonormal:

$$\langle \phi_r \, | \, \phi_s \rangle = \delta_{r,s} \, . \qquad (2.5)$$

Thus, the Hamiltonian is equally well the electronic Hamiltonian for the neutral

$$\hat{H} \Psi_I^{(n)} = E_I^{(n)} \Psi_I^{(n)}, \qquad (2.6)$$

the cation,

$$\hat{H} \Psi_I^{(n-1)} = E_I^{(n-1)} \Psi_I^{(n-1)}, \qquad (2.7)$$

and the anion

$$\hat{H} \Psi_I^{(n+1)} = E_I^{(n+1)} \Psi_I^{(n+1)}. \qquad (2.8)$$

The parent wave function $\Psi_0(n)$ will be referred to as the "target."

The QPE solutions are of two types. The ionization potential (IP) QPE eigenvalues are

$$\omega = E_0^{(n)} - E_I^{(n-1)}, \qquad (2.9)$$

whereas the electron affinity (EA) QPE eigenvalues are

$$\omega = E_I^{(n+1)} - E_0^{(n)}. \qquad (2.10)$$

These are simply orbital energies in the independent electron approximation. More generally, they are the negative of the IPs and EAs. In the solid-state limit, the excitation energies of the solid with one more or one less electron may be expressed in terms of these electron addition and removal energies and the chemical potential ([22], p. 75).

The eigenfunctions of the QPE are "generalized overlaps." They may be thought of as the wave functions for particle and hole states. Such states are clearly canonical spin orbitals in the independent electron model. The proper definition for interacting electrons is as follows: We can always write (using the numeral j to stand for the space and spin coordinates of the jth electron)

$$\Psi_0^{(n)}(1, 2, \ldots, n) = \frac{1}{\sqrt{n}} \sum_I \chi_I(1) \Psi_I^{(n-1)}(2, 3, \ldots, n) \qquad (2.11)$$

so that the Ith cation generalized overlap

$$\chi_I(1) = \sqrt{n} \int \Psi_I^{(n-1)*}(2,3,\ldots,n)\Psi_0^{(n)}(1,2,\ldots,n)\,d2\,d3\ldots dn$$

$$= \sum_i \langle \Psi_I^{(n-1)}|\hat{a}_i|\Psi_0^{(n)}\rangle \phi_i(1) \qquad (2.12)$$

is $\sqrt{n}$ times the probability amplitude for the remaining electron when $(n-1)$ electrons are detected in the Ith cation electronic state. The Ith anion generalized overlap is similarly defined as

$$\chi_I(1) = \sqrt{n+1} \int \Psi_0^{(n)*}(2,3,\ldots,n+1)\Psi_I^{(n+1)}(1,2,\ldots,n+1)\,d2\,d3\ldots d(n+1)$$

$$= \sum_i \langle \Psi_0^{(n)}|\hat{a}_i|\Psi_I^{(n+1)}\rangle \phi_i(1)\,. \qquad (2.13)$$

Although the "close-coupling" expansion of Eq. (2.11) is convenient for interpretational purposes, the coupling between the cation states makes it unsuitable for deriving a quasi-particle equation that does not explicitly involve final states. Instead, we will use the configuration interaction (CI) expansion,

$$\Psi^{(n-1)} = \sum_i c_i^* \hat{a}_i \Psi_0^{(n)} + \sum_I c_I^* \Xi_I^{(n-1)}, \qquad (2.14)$$

where we have assumed

$$\langle \Xi_I^{(n-1)}|\hat{a}_i|\Psi_0^{(n)}\rangle = 0 \qquad (2.15)$$

for all values of i and I, and

$$\langle \Xi_I^{(n-1)}|\Xi_J^{(n-1)}\rangle = \delta_{I,J} \qquad (2.16)$$

for all values of I and J, for the sake of simplicity. Hence, the expansion coefficient of the generalized overlap in the spin orbital basis set is

$$x_i \equiv \langle \phi_i|\chi\rangle = \langle \Psi^{(n-1)}|\hat{a}_i|\Psi_0^{(n)}\rangle = \sum_j \gamma_{i,j} c_j, \qquad (2.17)$$

where

$$\gamma_{i,j} = \langle \Psi_0^{(n)}|\hat{a}_j^\dagger \hat{a}_i|\Psi_0^{(n)}\rangle \qquad (2.18)$$

is the (one-electron reduced) density matrix.

(Equation 2.17 implies that all the components of the generalized overlaps are zero along the unoccupied natural spin orbitals of the parent. An easy way to verify this is to choose the underlying spin orbital basis to be the spin orbitals that diagonalize the density matrix [i.e., the natural spin orbitals]. It then follows that

$$|x_i|^2 = |\langle \Psi^{(n-1)}|\hat{a}_i|\Psi_0^{(n)}\rangle|^2 \le \langle \Psi_0^{(n)}|\hat{a}_i^\dagger \hat{a}_i|\Psi_0^{(n)}\rangle \langle \Psi^{(n-1)}|\Psi^{(n-1)}\rangle = \gamma_{i,i}, \qquad (2.19)$$

so that nonzero components of the generalized overlap are only allowed for natural spin orbitals with nonzero occupation number $\gamma_{i,i}$.)

The corresponding anion equations are

$$\Psi^{(n+1)} = \sum_i c_i \hat{a}_i^\dagger \Psi_0^{(n)} + \sum_I c_I \Xi_I^{(n+1)}, \tag{2.20}$$

$$\langle \Psi_0^{(n)} | \hat{a}_i | \Xi_I^{(n+1)} \rangle = 0, \tag{2.21}$$

$$\langle \Xi_I^{(n+1)} | \Xi_J^{(n+1)} \rangle = \delta_{I,J}, \tag{2.22}$$

$$x_i = \langle \phi_i | \chi \rangle = \langle \Psi_0^{(n)} | \hat{a}_i | \Psi^{(n+1)} \rangle = \sum_j \bar{\gamma}_{i,j} c_j, \tag{2.23}$$

and

$$\bar{\gamma}_{i,j} = \langle \Psi_0^{(n)} | \hat{a}_i \hat{a}_j^\dagger | \Psi_0^{(n)} \rangle = \delta_{i,j} - \gamma_{i,j}. \tag{2.24}$$

The solutions to the QPE give spectroscopic information. The eigenvalues are IPs and EAs, whereas the generalized overlaps give scattering information. More specifically, the magnitudes of the IP generalized overlaps (called "spectroscopic factors") are used to estimate relative intensities in photoelectron binding energy spectra [3] and the spherically averaged momentum distributions of IP generalized overlaps are proportional to the triple differential cross sections for high-energy high-momentum-transfer symmetric binary $(e, 2e)$ scattering (also referred to as "electron momentum spectroscopy") [24]. Summation conditions may be used to calculate the density matrix

$$\gamma_{i,j} = \sum_{\substack{cation\ states\ I}} x_i^{(I)} x_j^{(I)*} \tag{2.25}$$

and total energy

$$E_0^{(n)} = \frac{1}{2} \sum_{\substack{cation\ states\ I \\ i,j}} x_i^{(I)*} (\omega_I \delta_{i,j} + h_{i,j}) x_j^{(I)} \tag{2.26}$$

of the target state (Appendix A).

The EA generalized overlaps are stationary-state solutions for the low-energy electron-molecule scattering problem [13]. We therefore anticipate that the QPE will reflect the dynamics of scattering electrons. More specifically, the Hamiltonian should be the sum of the kinetic energy of the electron, a nuclear attraction term, Coulomb and exchange terms, and a self-energy term describing many-body effects such as correlation and relaxation (or polarization). Similar expectations apply to the IP generalized overlaps, provided we agree to regard them as solutions of the problem of a "hole" scattering with a molecule.

3. Wave-Function Quasi-Particle Equation

The derivation of the wave-function quasi-particle equation (QPE) proceeds from the groundwork laid in Section 2 by forming a matrix equation and then applying standard partitioning techniques (Appendix B). We identify the configuration interaction (CI) self-energy by analogy with the Green function QPE. The

clarification of the precise relationship of this wave-function QPE with the usual Green function QPE will be delayed until Section 4.

We must begin with an equation whose eigenvalues are minus the ionization potentials. Because of the complex conjugate relationship between the coefficients of the cation wave function and its generalized overlap, we begin with

$$\langle \Psi^{(n-1)} | (E_0^{(n)} - \hat{H}) = \omega \langle \Psi^{(n-1)} |. \tag{3.1}$$

We chose a basis that is partitioned into functions spanning a primary space (P) and a secondary space (Q):

$$P \longleftrightarrow \{\hat{a}_j \Psi_0^{(n)}\}$$

$$Q \longleftrightarrow \{\Xi_I^{(n-1)}\}. \tag{3.2}$$

Right multiplication of Eq. (3.1) gives

$$\begin{bmatrix} \mathbf{K}^{P,P} & \mathbf{K}^{P,Q} \\ \mathbf{K}^{Q,P} & \mathbf{K}^{Q,Q} \end{bmatrix} \begin{pmatrix} \mathbf{c}^P \\ \mathbf{c}^Q \end{pmatrix} = \omega \begin{bmatrix} \gamma & \mathbf{0} \\ \mathbf{0} & 1 \end{bmatrix} \begin{pmatrix} \mathbf{c}^P \\ \mathbf{c}^Q \end{pmatrix}, \tag{3.3}$$

where

$$K_{i,j}^{P,P} = \langle \Psi_0^{(n)} | \hat{a}_j^\dagger (E_0^{(n)} - \hat{H}) \hat{a}_i | \Psi_0^{(n)} \rangle$$

$$= \langle \Psi_0^{(n)} | [\hat{H}, \hat{a}_j^\dagger] \hat{a}_i | \Psi_0^{(n)} \rangle$$

$$= \sum_p \gamma_{i,p} h_{p,j} + \frac{1}{2} \sum_{p,q,t} \langle \Psi_0^{(n)} | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_t \hat{a}_i | \Psi_0^{(n)} \rangle v_{pq,jt}, \tag{3.4}$$

$$K_{I,j}^{Q,P} = \langle \Psi_0^{(n)} | \hat{a}_j^\dagger (E_0^{(n)} - \hat{H}) | \Xi_I^{(n-1)} \rangle$$

$$= \langle \Psi_0^{(n)} | [\hat{H}, \hat{a}_j^\dagger] | \Xi_I^{(n-1)} \rangle, \tag{3.5}$$

$$K_{i,J}^{P,Q} = \langle \Xi_J^{(n-1)} | (E_0^{(n)} - \hat{H}) \hat{a}_i | \Psi_0^{(n)} \rangle$$

$$= \langle \Xi_J^{(n-1)} | [\hat{a}_i, \hat{H}] | \Psi_0^{(n)} \rangle, \tag{3.6}$$

and

$$K_{I,J}^{Q,Q} = \langle \Xi_J^{(n-1)} | (E_0^{(n)} - \hat{H}) | \Xi_I^{(n-1)} \rangle$$

$$= E_0^{(n)} \delta_{I,J} - H_{J,I}^{Q,Q}. \tag{3.7}$$

Hence (Appendix B), we obtain a QPE,

$$[\mathbf{K}^{P,P} + \mathbf{K}^{P,Q} (\omega \mathbf{1}^{Q,Q} - \mathbf{K}^{Q,Q})^{-1} \mathbf{K}^{Q,P}] \mathbf{c}^P = \omega \gamma \mathbf{c}^P, \tag{3.8}$$

whose eigenvalues

$$\omega = E_0^{(n)} - E^{(n-1)} \tag{3.9}$$

are minus the ionization potentials of the parent and whose eigenvectors give the corresponding generalized overlaps:

$$\mathbf{x} = \gamma \mathbf{c}^P. \tag{3.10}$$

This QPE may be interpreted as follows: It is the matrix form of a one-electron Schrödinger equation consisting of a "zero-order" part $K^{P,P}$ and what we will call the "(particle-hole) conjugate Feshbach optical potential" in analogy with [13]:

$$\bar{\mathbf{V}}^{\text{OPT}}(\omega) = \mathbf{K}^{P,Q}(\omega\mathbf{1}^{Q,Q} - \mathbf{K}^{Q,Q})^{-1}\mathbf{K}^{Q,P}. \tag{3.11}$$

The zero-order part is (the adjoint of) the Hamiltonian in the so-called extended Koopmans' theorem method [25–29]. It accounts for (some) correlation but no relaxation effects by describing the cation wave function as the parent wave function with an unrelaxed "hole" in the space of occupied natural spin orbitals. Hence, the conjugate Feshbach optical potential describes relaxation effects (including changes in correlation due to relaxation).

Since both correlation and relaxation are normally relegated to the Green function self-energy and in analogy with the Green function QPE, we rewrite the wave-function QPE as

$$[\mathbf{F} + \mathbf{\Sigma}^{\text{cl}}(\omega)]\mathbf{c}^P = \omega\mathbf{c}^P, \tag{3.12}$$

where

$$F_{i,j} = \langle \Psi_0^{(n)} | \{[\hat{H}, \hat{a}_j^\dagger], \hat{a}_i\} | \Psi_0^{(n)} \rangle$$

$$= h_{i,j} + \sum_{p,q,t} v_{ip,jq}\gamma_{q,p} \tag{3.13}$$

is a generalized Fock operator and

$$\Sigma_{i,j}^{\text{cl}}(\omega) = \bar{\mathbf{V}}_{i,j}^{\text{OPT}}(\omega) + \omega\bar{\gamma}_{i,j} - \langle \Psi_0^{(n)} | \hat{a}_i [\hat{H}, \hat{a}_j^\dagger] | \Psi_0^{(n)} \rangle \tag{3.14}$$

is the "self-energy." By construction, the first term in the self-energy accounts for relaxation effects (including correlation changes due to relaxation), whereas the remaining terms account for correlation effects. The second term comes from applying Eq. (2.24).

The primary advantage of the QPE (3.12) over the QPE (3.8) is simple. It is only necessary to approximate the self-energy, because the primary many-body effects have been relegated to the self-energy. Those many-body effects that do appear in the generalized Fock operator are in the density matrix and so may be treated through the self-consistency condition given in Eq. (2.25), in analogy with ordinary Hartree–Fock.

4. Equations-of-Motion Derivation

The best way to understand the relationship between the proposed wave function and traditional Green function quasi-particle equations (QPEs) is to derive them both within a single formalism. We will do this using the equations-of-motion (EOM) formalism.

Briefly, the EOM formalism [8, 30] solves the EOM

$$\tilde{L}\hat{O}^\dagger \equiv [\hat{H}, \hat{O}^\dagger] = \omega\hat{O}^\dagger \tag{4.1}$$

($\tilde{L}$ is the Liouvillian superoperator) as a matrix problem by introducing an operator basis set and the metric

$$(\hat{A}^\dagger \mid \hat{B}^\dagger) \equiv \langle \Psi_0^{(n)} | \{\hat{A}, \hat{B}^\dagger\} | \Psi_0^{(n)} \rangle. \tag{4.2}$$

The solutions

$$\hat{O}^\dagger = |\Psi^{(n+1)}\rangle\langle\Psi_0^{(n)}|; \qquad \omega = E^{(n+1)} - E_0^{(n)} \tag{4.3}$$

and

$$\hat{O}^\dagger = |\Psi_0^{(n)}\rangle\langle\Psi^{(n-1)}|; \qquad \omega = E_0^{(n)} - E^{(n-1)} \tag{4.4}$$

will be obtained for an "EOM complete" basis set [8] of (composite) particle creation operators. (Note that the Fock space inner products $\langle\Psi^{(n+1)}|\Psi_0^{(n)}\rangle = \langle\Psi^{(n-1)}|\Psi_0^{(n)}\rangle = 0$.) The canonical choice of basis set consists of combinations of creation and annihilation operators [31, 32] (e.g., $\hat{a}_r^\dagger$ and $\hat{a}_a^\dagger\hat{a}_b^\dagger\hat{a}_i$), but combinations of creation operators and ket-bra "state-transfer operators" (e.g., $\hat{a}_r^\dagger|\Psi_1^{(n)}\rangle\langle\Psi_0^{(n)}|$) have also been used [33].

The solution of the matrix EOM need not be equivalent to solving the matrix versions of the $(n \pm 1)$-electron Schrödinger equations (2.7) and (2.8) when the target wave function is exact but the operator basis set is incomplete. However, we prove an original theorem in Appendix C providing conditions on the operator basis set for which the EOM method becomes equivalent to the wave-function method.

QPEs whose eigenvalues are minus the ionization potentials and electron affinities may be derived from the EOM for operator basis sets that partition as

$$P \longrightarrow \{\hat{a}_i^\dagger\}$$
$$Q \longrightarrow \{\hat{A}_i^\dagger\}. \tag{4.5}$$

The partitioned EOM is

$$\begin{bmatrix} \mathbf{F} & \mathbf{L}^{P,Q} \\ \mathbf{L}^{Q,P} & \mathbf{L}^{Q,Q} \end{bmatrix} \begin{pmatrix} \mathbf{d}^P \\ \mathbf{d}^Q \end{pmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{S}^{P,Q} \\ \mathbf{S}^{Q,P} & \mathbf{S}^{Q,Q} \end{bmatrix} \begin{pmatrix} \mathbf{d}^P \\ \mathbf{d}^Q \end{pmatrix}, \tag{4.6}$$

with the generalized Fock operator $\hat{\mathbf{F}}$ defined by Eq. (3.13) and

$$S_{i,j}^{P,Q} = (\hat{a}_i^\dagger \mid \hat{A}_j^\dagger) = (S_{j,i}^{Q,P})^*,$$
$$S_{i,j}^{Q,Q} = (\hat{A}_i^\dagger \mid \hat{A}_j^\dagger). \tag{4.7}$$

Hence (Appendix B),

$$[\mathbf{F} + \Sigma^{\text{EOM}}(\omega)]\mathbf{d}^P = \omega\mathbf{d}^P;$$

$$\Sigma^{\text{EOM}}(\omega) = (\mathbf{L}^{P,Q} - \omega\mathbf{S}^{P,Q})(\omega\mathbf{S}^{Q,Q} - \mathbf{L}^{Q,Q})^{-1}(\mathbf{L}^{Q,P} - \omega\mathbf{S}^{Q,P}). \tag{4.8}$$

In general, there is no simple relationship between $\mathbf{d}^P$ and the coefficients $\mathbf{x}$ of the generalized overlap except for particular operator basis sets. One choice will yield the CI QPE and $\mathbf{d}^P = \mathbf{c}^P$ [see Eq. (3.10)], whereas another choice will yield the Green function QPE and $\mathbf{d}^P = \mathbf{x}$.

The CI QPE is easily derived, knowing the conditions under which EOM and CI become equivalent. According to Appendix C, the solutions of the $(n - 1)$-electron CI equation (3.3) should be included among the solutions of the EOM (4.6) by the choice

$$\{\hat{A}_I^\dagger\} = \{|\Psi_0^{(n)}\rangle\langle\Xi_I^{(n-1)}|\} \cup \{\hat{a}_i^\dagger|\Psi_0^{(n)}\rangle\langle\Psi_0^{(n)}|\}. \tag{4.9}$$

It is then easily verified that

$$\Sigma^{\text{EOM}}(\omega) = \Sigma^{CI}(\omega). \tag{4.10}$$

The Green function self-energy may be defined through the Dyson equation

$$\Sigma^{\text{GF}}(\omega) \equiv \omega - \mathbf{F} - \mathbf{G}^{-1}(\omega), \tag{4.11}$$

where $\mathbf{G}(\omega)$ is the exact Green function. It can be shown [11] that $\Sigma^{\text{EOM}}(\omega) = \Sigma^{\text{GF}}(\omega)$ for operator basis sets where $\mathbf{S}^{P,Q} = \mathbf{0}$. This case is approached in the CI QPE derivation only when the orbital basis is restricted to natural spin orbitals with occupancy numbers near unity ($\mathbf{S}^{P,Q} = \mathbf{1} - \gamma$). Zeroing the off-diagonal blocks of the overlap matrix may, however, be achieved by the choice

$$\{\hat{A}_I^\dagger\} = \{|\Psi_0^{(n)}\rangle\langle\Xi_I^{(n-1)}|\} \cup \{|\Xi_I^{(n+1)}\rangle\langle\Psi_0^{(n)}|\} \tag{4.12}$$

with orthonormality conditions given by Eqs. (2.15), (2.16), (2.21), and (2.22). With this choice,

$$\Sigma^{\text{GF}}(\omega) = \Sigma^{\text{EOM}}(\omega) = \mathbf{V}^{\text{OPT}}(\omega) + \overline{\mathbf{V}}^{\text{OPT}}(\omega), \tag{4.13}$$

where the conjugate Feshbach optical potential $\overline{\mathbf{V}}^{\text{OPT}}(\omega)$ was defined in Eq. (3.11) and the "Feshbach optical potential"

$$\mathbf{V}^{\text{OPT}}(\omega) = \overline{\mathbf{K}}^{P,Q}(\omega\mathbf{1}^{Q,Q} - \overline{\mathbf{K}}^{Q,Q})^{-1}\overline{\mathbf{K}}^{Q,P} \tag{4.14}$$

appears with

$$\overline{K}_{i,J}^{P,Q} = \langle\Psi_0^{(n)}|[\hat{a}_i, \hat{H}]|\Xi_J^{(n+1)}\rangle, \tag{4.15}$$

$$\overline{K}_{I,j}^{Q,P} = \langle\Xi_I^{(n+1)}|[\hat{H}, \hat{a}_j^\dagger]|\Psi_0^{(n)}\rangle, \tag{4.16}$$

and

$$\overline{K}_{I,J}^{Q,Q} = \langle\Xi_I^{(n+1)}|\hat{H}|\Xi_J^{(n+1)}\rangle - E_0^{(n)}\delta_{I,J}. \tag{4.17}$$

Thus, relaxation effects are described by $\overline{\mathbf{V}}^{\text{OPT}}(\omega)$ in both the $\Sigma^{CI}(\omega)$ and $\Sigma^{\text{GF}}(\omega)$ but correlation effects are treated differently.

It should be emphasized that the classic Green function approach uses a different operator basis set than the one used above. The classic Green function basis set is completely composed of combinations of creation and annihilation operators. We have taken a considerable step toward a wave-function treatment by introducing ket-bra operators to arrive at Eq. (4.13) for the self-energy. Such an approach is normally avoided in practical applications of the Green function method because of a delicate cancellation of errors that occurs when second-quantized operators are used. (More specifically, there is a reduction in the order of the reduced density matrices entering into the EOM when second-quantized

operators are used [30].) Indeed, the Green function self-energy given in Eq. (4.13) has no obvious computational advantage over the simpler CI self-energy.

To summarize, we have shown more precisely the sense in which the CI self-energy is a self-energy; that is, $\Sigma^{\mathrm{CI}}(\omega)$ plays the same role in the partitioning of the EOM as does $\Sigma^{\mathrm{GF}}(\omega)$. They are, however, not identical because they refer to different operator basis sets and lead to different eigenfunctions.

5. Self-Energy Approximations

Practical quasi-particle equation (QPE) calculations involve approximate self-energies, and the wave-function formalism is no different from the Green function formalism in this respect. In principle, approximating the CI self-energy is just a matter of choosing an approximate wave function and a suitable set of cation basis functions. However, the Green function QPE formalism is well developed for conventional closed-shell bound-state ionization potential calculations and can be used as a guide in constructing self-energy approximations for use in the CI QPE. We illustrate the basic idea by deriving a wave-function analog of the Green function two-particle-hole Tamm–Dancoff approximation ($2ph$-TDA) [34]. This should also help to further clarify the relationship between the CI and Green function quasi-particle equations.

We will assume that the self-energy calculation has been preceded by a Hartree–Fock (HF) calculation on the parent. This yields a ground-state wave function $\Phi_0^{(n)}$ and sets of occupied and virtual spin orbitals whose energies we shall denote by ε_r for orbital r. The index convention

$$\{a, b, \ldots, g, h\} \longleftrightarrow \text{virtual spin orbitals}$$

$$\{i, j, \ldots, m, n\} \longleftrightarrow \text{occupied spin orbitals}$$

$$\{o, p, \ldots, y, z\} \longleftrightarrow \text{either type of spin orbital} \qquad (5.1)$$

will be adhered to throughout this section.

The $2ph$-TDA results from the equations-of-motion formalism when [35] (1) the exact target wave function is replaced by the HF ground state, and (2) the operator basis set consists of 2-hole/1-particle operators $\{\hat{a}_j^\dagger \hat{a}_i^\dagger \hat{a}_a\}$ and 1-hole/2-particle operators $\{\hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_i\}$ in addition to the usual 1-hole $\{\hat{a}_j^\dagger\}$ and 1-particle $\{\hat{a}_a^\dagger\}$ operators. The resultant self-energy is given by Eq. (4.13),

$$\bar{V}_{r,s}^{\mathrm{OPT}}(\omega) = \frac{1}{2} \sum_{i,j,a} \frac{v_{ra,ij} v_{ij,sa}}{\omega + \varepsilon_a - \varepsilon_i - \varepsilon_j - v_{ja,ja} - v_{ia,ia} + v_{ij,ij}}, \qquad (5.2)$$

and

$$V_{r,s}^{\mathrm{OPT}}(\omega) = \frac{1}{2} \sum_{a,b,i} \frac{v_{ri,ab} v_{ab,si}}{\omega + \varepsilon_i - \varepsilon_a - \varepsilon_b + v_{ai,ai} + v_{bi,bi} - v_{ab,ab}} \qquad (5.3)$$

in the B_k approximation (Appendix B).

An obvious approach [34] to approximating the CI self-energy is once again to approximate the target wave function by the HF wave function $\Phi_0^{(n)}$ and to treat

the ion as a linear combination of 1-hole states $\{\hat{a}_i \Phi_0^{(n)}\}$ and 2-hole/1-particle states $\{\hat{a}_a^\dagger \hat{a}_j \hat{a}_i \Phi_0^{(n)}\}$. This gives

$$\Sigma_{k,l}^{\text{CI}}(\omega) = \frac{1}{2} \sum_{i,j,a} \frac{v_{ka,ij} v_{ij,la}}{\omega + \varepsilon_a - \varepsilon_i - \varepsilon_j - v_{ja,ja} - v_{ia,ia} + v_{ij,ij}} \qquad (5.4)$$

in the B_k approximation; that is, $\Sigma^{\text{CI}}(\omega)$ coincides with the occupied orbital block of $\overline{\mathbf{V}}^{\text{OPT}}(\omega)$ as given in Eq. (5.2) and the other terms in the self-energy equation (3.14) are zero.

However, this CI self-energy must contain error terms that are second-order in Møller-Plesset perturbation theory (MPPT) [36] since it would otherwise lead to errors in the second-order expressions for the ionization potentials and for the generalized overlaps [12, 37]. The errors may be corrected by introducing the first-order wave function

$$\Psi_0^{(n)} = \left[1 + \frac{1}{4} \sum_{a,b,k,l} \frac{v_{ab,kl}}{\varepsilon_k + \varepsilon_l - \varepsilon_a - \varepsilon_b} \hat{a}_b^\dagger \hat{a}_l \hat{a}_a^\dagger \hat{a}_k \right] \Phi_0^{(n)} \qquad (5.5)$$

into the correlation term and gathering the parts that are second-order in the fluctuation potential. We obtain

$$-\langle \Psi_0^{(n)} | \hat{a}_i [\hat{H}, \hat{a}_j^\dagger] | \Psi_0^{(n)} \rangle = \frac{1}{2} \sum_{a,b,k} \frac{v_{ik,ab} v_{ab,jk}}{\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b} - \frac{1}{2} \varepsilon_j \sum_{a,b,k}$$

$$\times \frac{v_{ik,ab} v_{ab,jk}}{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b)}. \qquad (5.6)$$

The first sum is the second-order part of the Feshbach optical potential. The second sum cancels with the second-order part of

$$\omega \overline{\gamma}_{i,j} = \varepsilon_j \frac{1}{2} \sum_{a,b,k} \frac{v_{ik,ab} v_{ab,jk}}{(\varepsilon_i + \varepsilon_k - \varepsilon_a - \varepsilon_b)(\varepsilon_j + \varepsilon_k - \varepsilon_a - \varepsilon_b)}. \qquad (5.7)$$

The sum of Eqs. (5.4), (5.6), and (5.7) constitutes a $2ph$-TDA-like approximation for the CI self-energy that we expect to be similar in quality to the $2ph$-TDA when used in the diagonal approximation (Appendix B) to calculate inner and outer valence ionization energy spectra.

The foregoing analysis is not meant to imply that a higher-quality target wave function should always be used to calculate the "correlation terms" than is used to calculate the "relaxation term" (conjugate Feshbach optical potential) in the CI self-energy. However, the use of different targets for the two terms would be consistent with the spirit of "frozen orbital" [38] or "unrelaxed" [8] CI where the reference (target) wave function in the ion CI expansion is of lower quality than is the parent CI wave function.

6. Conclusion

The Green function method is a traditional way to reformulate an n-electron problem as a one-electron quasi-particle equation (QPE) involving a pseudopotential (the self-energy) that describes the principal many-body effects. Such an ap-

proach is desirable for comparison with other one-electron equations (e.g., in density functional theory), where the prior existence of a phenomenological one-electron equation may give insight into self-energy approximations (e.g., in solid-state and scattering applications) or simply because of computational advantages arising from working with a lower dimensional equation. However, difficulties arise in some applications of the QPE because the operator nature of Green functions makes it difficult to recover a wave-function formulation when this is needed or desired for interpretational reasons (e.g., to separate correlation and relaxation effects [12]) or computational convenience (e.g., to implement matrix element evaluation techniques originally developed for wave-function methods [16, 17]) or both (e.g., to separate open and closed channels in low-energy electron-molecule scattering [13, 14]).

We have proposed a configuration interaction (CI) wave-function QPE as an alternative to the usual Green function QPE for applications where a clear connection with an underlying wave-function formulation is desired. Our CI QPE may be regarded as an extension of historical developments in low-energy electron-molecule scattering. It differs from these historical treatments by maintaining a closer analogy with the Green function QPE. Thus, we have chosen to maintain the eigenvalue and eigenfunction character of the Green function QPE as much as possible in deriving the CI QPE. At the same time, the final CI QPE is not the same as the Green function QPE, and this point has been made clear by deriving the two QPEs within the equations-of-motion formalism where they can be more readily compared. Although we have restricted our development to ionization, the modifications required to treat electron attachment and scattering calculations are straightforward.

Practical applications of either QPE require the use of self-energy approximations. In principle, this is merely a matter of choosing an approximate target wave function and a suitable set of ion wave functions as a basis set. In practice, it may be desirable to use a different target wave function for the "relaxation" and "correlation" terms in the CI self-energy. We have emphasized similarities and differences between the Green function and CI QPEs by deriving a $2ph$-TDA-like CI self-energy approximation that we expect to be useful for calculating inner and outer valence ionization spectra.

However, the development of and investigation of practical CI self-energy approximations was not the primary objective of the present paper. Instead, our objective was show that a Green function-like QPE could be developed within a wave-function formalism. The further development of CI self-energy approximations should help to make the CI QPE a useful alternative to the Green function QPE for one-electron reformulations of many-electron problems.

Appendix A: Summation Conditions

Proof of Eq. (2.25)

$$\sum_{\substack{\text{cation states } I}} x_j^{(I)*} x_i^{(I)} = \sum_I \langle \Psi_0^{(n)} | \hat{a}_j^\dagger | \Psi_I^{(n-1)} \rangle \langle \Psi_I^{(n-1)} | \hat{a}_i | \Psi_0^{(n)} \rangle$$

$$= \langle \Psi_0^{(n)} | a_j^\dagger \hat{a}_i | \Psi_0^{(n)} \rangle = \gamma_{i,j}. \tag{A.1}$$

Proof of Eq. (2.26)

$$\sum_{\substack{\text{cation states } l \\ i,j}} x_j^{(l)*}[\omega_I \delta_{i,j} + h_{i,j}]x_j^{(l)} \tag{A.2}$$

$$= \sum_{l,i,j} \langle \Psi_0^{(n)}|\hat{a}_i^\dagger|\Psi_I^{(n-1)}\rangle \langle \Psi_I^{(n-1)}|[(E_0^{(n)} - E_I^{(n-1)})\delta_{i,j} + h_{i,j}]\hat{a}_j|\Psi_0^{(n)}\rangle \tag{A.3}$$

$$= \sum_{l,i,j} \langle \Psi_0^{(n)}|\hat{a}_i^\dagger|\Psi_I^{(n-1)}\rangle \langle \Psi_I^{(n-1)}|[\hat{a}_j, \hat{H}]\delta_{i,j} + h_{i,j}\hat{a}_j|\Psi_0^{(n)}\rangle \tag{A.4}$$

$$= \sum_{i,j} \langle \Psi_0^{(n)}|\hat{a}_i^\dagger([\hat{a}_j, \hat{H}]\delta_{i,j} + h_{i,j}\hat{a}_j)|\Psi_0^{(n)}\rangle \tag{A.5}$$

$$= \sum_{i,j} \langle \Psi_0^{(n)}|\hat{a}_i^\dagger\left[\left(\sum_p h_{j,p}\hat{a}_p + \frac{1}{2}\sum_{t,p,q} v_{jt,pq}\hat{a}_t^\dagger\hat{a}_q\hat{a}_p\right)\delta_{i,j} + h_{i,j}\hat{a}_j\right]|\Psi_0^{(n)}\rangle \tag{A.6}$$

$$= 2\langle \Psi_0^{(n)}|\hat{h} + \hat{v}|\Psi_0^{(n)}\rangle = 2E_0^{(n)}. \tag{A.7}$$

Appendix B: Partitioning Theory

Löwdin partitioning [39] is a method that makes large matrix eigenvalue problems more tractable by reducing their dimensionality. Consider a matrix eigenvalue problem involving a "Hamiltonian" $\mathbf{H}$, "overlap matrix" $\mathbf{S}$, and eigenvector $\mathbf{c}$, which has been partitioned into a blocks corresponding to primary (P) and secondary (Q) spaces:

$$\begin{bmatrix} \mathbf{H}^{P,P} & \mathbf{H}^{P,Q} \\ \mathbf{H}^{Q,P} & \mathbf{H}^{Q,Q} \end{bmatrix} \begin{pmatrix} \mathbf{c}^P \\ \mathbf{c}^Q \end{pmatrix} = \omega \begin{bmatrix} \mathbf{S}^{P,P} & \mathbf{S}^{P,Q} \\ \mathbf{S}^{Q,P} & \mathbf{S}^{Q,Q} \end{bmatrix} \begin{pmatrix} \mathbf{c}^P \\ \mathbf{c}^Q \end{pmatrix}. \tag{B.1}$$

Then, we can solve for the P-block of the $\mathbf{c}$ vector to obtain

$$[\mathbf{H}^{P,P} + M(\omega)]\mathbf{c}^P = \omega\mathbf{S}^{P,P}\mathbf{c}^P;$$

$$M(\omega) = (\mathbf{H}^{P,Q} - \omega\mathbf{S}^{P,Q})(\omega\mathbf{S}^{Q,Q} - \mathbf{H}^{Q,Q})^{-1}(\mathbf{H}^{Q,P} - \omega\mathbf{S}^{Q,P}). \tag{B.2}$$

The dimensionality of the original eigenvalue problem [Eq. (B.1)] has now been reduced to that of an eigenvalue problem in the primary space. Equation (B.2) must, however, be solved in either an iterative or "graphical" manner by repeatedly constructing and then diagonalizing $\mathbf{H}^{P,P} + M(\omega)$ for different values of ω. Therefore, the relative value of solving Eq. (B.1) versus Eq. (B.2) depends on the number of solutions required and the quality of any initial estimates of ω. Once Eq. (B.2) is solved, proper normalization of $\mathbf{c}^P$ may be obtained from the derivative of $\mathbf{M}(\omega)$

$$\frac{\mathbf{c}^{P\dagger}\mathbf{S}^{P,P}\mathbf{c}^P}{\mathbf{c}^\dagger\mathbf{S}\mathbf{c}} = \left[1 - \frac{\mathbf{c}^{P\dagger}\frac{\partial\mathbf{M}(\omega)}{\partial\omega}\mathbf{c}^P}{\mathbf{c}^{P\dagger}\mathbf{S}^{P,P}\mathbf{c}^P}\right]^{-1} \tag{B.3}$$

without first calculating $\mathbf{c}^Q$.

Several common useful approximations on the basic equation (B.2) have been made in the literature for the case when $S = 1$. We list these briefly along with any restrictions on their appropriateness.

Diagonal Approximation

When

$$\mathbf{H}^{P,P}\mathbf{d}^{P} = \omega^{P}\mathbf{d}^{P} \qquad (\text{B.4})$$

is a good zero-order approximation to the complete solution of Eq. (B.1), then

$$\omega^{P} + \mathbf{d}^{P\dagger}\mathbf{M}(\omega)\mathbf{d}^{P} \approx \omega. \qquad (\text{B.5})$$

Quasiparticle Approximation

When ω is far away from all solutions ω^{Q} of

$$\mathbf{H}^{Q,Q}\mathbf{d}^{Q} = \omega^{Q}\mathbf{d}^{Q}, \qquad (\text{B.6})$$

then

$$\mathbf{M}(\omega) \approx \mathbf{M}(\omega^{P}). \qquad (\text{B.7})$$

B_{k} Approximation [40]

When $\mathbf{H}^{Q,Q}$ is nearly diagonal,

$$H_{k,l}^{Q,Q} \approx H_{k,l}^{Q,Q}\delta_{k,l}. \qquad (\text{B.8})$$

(Of course, this becomes an exact method when the basis of the secondary space is chosen to be that which diagonalizes $\mathbf{H}^{Q,Q}$ [41].)

Appendix C: Equivalence of EOM and CI

Theorem

Suppose that (1) the target wave function $\Psi_{0}^{(n)}$ is exact, (2) $\{\hat{A}_{I}^{\dagger}\}$ is a finite basis set of operators for which the equations-of-motion (EOM) metric matrix

$$S_{I,J} = (\hat{A}_{I}^{\dagger} \mid \hat{A}_{J}^{\dagger}) \qquad (\text{C.1})$$

is invertible, and (3) the basis set divides into two disjoint "ionization" $\{\hat{B}_{I}^{\dagger}\}$ and "electron attachment" $\{\hat{C}_{I}^{\dagger}\}$ subsets satisfying the closure conditions

$$\hat{B}_{J}^{\dagger}|\Psi_{0}^{(n)}\rangle \in \text{span}\{\hat{C}_{I}^{\dagger}|\Psi_{0}^{(n)}\rangle\} \quad \text{for all } J \qquad (\text{C.2})$$

and

$$\langle\Psi_{0}^{(n)}|\hat{C}_{J}^{\dagger} \in \text{span}\{\langle\Psi_{0}^{(n)}|\hat{B}_{I}^{\dagger}\} \quad \text{for all } J \qquad (\text{C.3})$$

Then, every solution of the cation CI equation

$$\sum_{J} \langle\Psi_{0}^{(n)}|[\hat{H}, \hat{B}_{J}^{\dagger}]\hat{B}_{I}|\Psi_{0}^{(n)}\rangle c_{J} = \omega \sum_{J} \langle\Psi_{0}^{(n)}|\hat{B}_{J}^{\dagger}\hat{B}_{I}|\Psi_{0}^{(n)}\rangle c_{J} \quad \text{for all } I \qquad (\text{C.4})$$

or the anion CI equation

$$\sum_J \langle \Psi_0^{(n)} | \hat{C}_I [\hat{H}, \hat{C}_J^\dagger] | \Psi_0^{(n)} \rangle c_J = \omega \sum_J \langle \Psi_0^{(n)} | \hat{C}_I \hat{C}_J^\dagger | \Psi_0^{(n)} \rangle c_J \quad \text{for all } I \qquad \text{(C.5)}$$

corresponds to a unique solution of the equation-of-motion

$$\sum_J (\hat{A}_I^\dagger | [\hat{H}, \hat{A}_J^\dagger]) d_J = \omega \sum_J S_{I,J} d_J \quad \text{for all } I. \qquad \text{(C.6)}$$

Proof

The proof is by construction. Let

$$|\Psi^{(n+1)}\rangle = \sum_J \hat{C}_J^\dagger |\Psi_0^{(n)}\rangle c_J \qquad \text{(C.7)}$$

and consider solving the simultaneous equations

$$|\Psi^{(n+1)}\rangle = \sum_J \hat{A}_J^\dagger |\Psi_0^{(n)}\rangle d_J \qquad \text{(C.8)}$$

and

$$0 = \sum_J \langle \Psi_0^{(n)} | \hat{A}_J^\dagger d_J \qquad \text{(C.9)}$$

for the coefficients d_J. These may be replaced by the equivalent equations

$$\langle \Psi_0^{(n)} | \hat{A}_I | \Psi^{(n+1)}\rangle = \sum_J \langle \Psi_0^{(n)} | \hat{A}_I \hat{A}_J^\dagger | \Psi_0^{(n)}\rangle d_J \qquad \text{(C.10)}$$

and

$$0 = \sum_J \langle \Psi_0^{(n)} | \hat{A}_J^\dagger \hat{A}_I | \Psi_0^{(n)}\rangle d_J \qquad \text{(C.11)}$$

only because of the closure conditions. Adding Eqs. (C.10) and (C.11) then gives

$$\langle \Psi_0^{(n)} | \hat{A}_I | \Psi^{(n+1)}\rangle = \sum_J \langle \Psi_0^{(n)} | \{\hat{A}_I, \hat{A}_J^\dagger\} | \Psi_0^{(n)}\rangle d_J, \qquad \text{(C.12)}$$

which has a unique solution because the EOM metric matrix has been assumed to be invertible. It remains to show that this solution is also a solution of the EOM (C.6). Insertion into Eq. (C.6) and application of Eqs. (C.7), (C.8), and the "killer condition" Eq. (C.9) and gives

$$\sum_J \langle \Psi_0^{(n)} | \hat{A}_I [\hat{H}, \hat{C}_J^\dagger] | \Psi_0^{(n)}\rangle c_J = \omega \sum_J \langle \Psi_0^{(n)} | \hat{A}_I \hat{C}_J^\dagger | \Psi_0^{(n)}\rangle c_J \quad \text{for all } I, \qquad \text{(C.13)}$$

which reduces to the anion CI Eq. (C.5) because of the closure condition (C.2). The argument is not significantly different when beginning with the cation CI Eq. (C.4).

Corollary

Every solution of the EOM also corresponds to a solution of one of the two CI equations unless the two CI equations share a common eigenvalue. (Note that this is extremely unlikely since the stability condition $\Delta E > 0$ for the reaction $2M \rightarrow M^+ + M^-$ leads to IP > EA for all ionization potentials IP and all electron affinities EA.) Hence, Eq. (C.8) holds for any solution of the EOM.

Proof

As long as the two CI equations have no eigenvalue in common, the EOM solutions generated in the proof of the theorem constitute a complete set of linearly independent solutions of the EOM. Each nondegenerate solution of the EOM comes from a nondegenerate solution of one or the other of the two CI equations. Degenerate EOM solutions come from degenerate CI solutions.

Acknowledgments

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