Optimized Partitioning in PT: Application for the Equation of Motion Describing Ionization Processes

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ABSTRACT: In computing ionization potentials via perturbative solution of the equation of motion for the ionization operator, we apply the technique of "partitioning optimization" elaborated recently for the calculation of correlation energy. Sample calculations indicate that second-order results may improve if the partitioning is optimized.   © 2003 Wiley Periodicals, Inc. Int J Quantum Chem 92: 160–167, 2003

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Introduction

Accurate calculation of energy differences, especially excitation energies and ionization potentials, remains a challenge in computational chemistry [1]. It is in general accepted that direct methods are preferred to the so-called delta techniques, which evaluate these quantities as small differences of large numbers.

Direct formulae for excitation energies and ionization potentials can be derived by using the equation of motion (EOM) technique [2–4]. EOM schemes are closely related to electron propagator or Green's function techniques [4–7], and practically all of these methods apply perturbation theory (PT) to derive explicit formulae at a given order.

PT is based on splitting the Hamiltonian to a zero-order part and a perturbation. Recently [8, 9], we investigated the problem of repartitioning the Hamiltonian by level shift operators, and set the value of the level shift parameters by optimizing a first-order Ansatz. The resulting second-order corrections remained size consistent and showed a significant improvement as compared to those obtained in Møller–Plesset [10] or Epstein–Nesbet [11, 12] partitionings. In the new partitioning no third-order corrections appear, and higher-order corrections were proved to converge faster to the exact (infinite order) results on a few examples. We note

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that a somewhat different procedure for optimizing the partitioning in PT was also elaborated by Freed and coworkers [13].

In this article we investigate if a similar optimization of partitioning is possible when solving the EOM perturbatively for ionization potentials (IPs). We shall select the Hartree–Fock operator as an initial zero order, that is, we start from Koopmans' energies, and consider the second-order Dyson equation for the IPs. This latter correction provides better results than Koopmans' values, but it is known to be insufficiently accurate [14, 15]. The theoretical part of the article, summarizing the formalism and introducing the optimal partitioning, is followed by presenting two sample calculations on the IPs of water and the N_2 molecule.

PT for the EOM

When considering ionizations or excitations of a molecule one conveniently starts with the so-called equation of motion

$$[H, \Omega] = \omega\Omega \qquad (1)$$

that holds for the ionization (excitation) operator Ω connecting two eigenstates of H, Ψ_0 and Ψ_K, by

$$\Omega\Psi_0 = \Psi_K.$$

The ionization (excitation) energy is $\omega = E_K - E_0$. The fact that excitations and ionizations may be treated on an equal footing is due to the second quantized representation of the Hamiltonian. In the present work we are concerned with ionization energies, although this particular section applies to excitations as well.

Introducing the "super" Hamiltonian or Liouvillean $\mathcal{H}$, which is defined by its action on any operator A being $\mathcal{H}A = [H, A]$, one may rewrite Eq. (1) as [16, 17]

$$\mathcal{H}\Omega = \omega\Omega. \qquad (2)$$

This latter form stresses that ionization (excitation) operators are eigenfunctions of a superoperator defined over ordinary operators, and one gets the corresponding ionization (excitation) energy as an eigenvalue.

To be able to apply standard approximations to the solution of this eigenvalue problem, one needs

a scalar product among the operators that constitute the domain of $\mathcal{H}$. We return to the construction of such a product later and suppose for the moment that there exists one denoted by $(.|.)$, between the ionization (excitation) operators. Accordingly, bra- and ket vectors of the operator space will be denoted by $(.|$ and $|.)$.

To derive a perturbative series for ω, let us split the super Hamiltonian for a zero-order superoperator and a perturbation

$$\mathcal{H} = \mathcal{H}^0 + \mathcal{W} \qquad (3)$$

and suppose that the solutions of the zero-order problem

$$\mathcal{H}^0|\Omega^0) = \omega^0|\Omega^0)$$

are known. Expanding the exact ionization energy ω to a Brillouin–Wigner perturbation series, one gets the super counterpart of the well-known sequence [18]

$$\omega = \omega^0 + (\Omega^0|\mathcal{W}|\Omega^0) + (\Omega^0|\mathcal{W}\mathcal{Q}^0(\omega)\mathcal{W}|\Omega^0)$$
$$+ (\Omega^0|\mathcal{W}\mathcal{Q}^0(\omega)\mathcal{W}\mathcal{Q}^0(\omega)\mathcal{W}|\Omega^0) + \mathcal{O}(4), \quad (4)$$

where the reduced resolvent is

$$\mathcal{Q}^0(z) = [P(zI - \mathcal{H}^0)]^{-1}P,$$

P being defined as

$$P = I - O$$

with

$$O = |\Omega^0)(\Omega^0|$$

and the unity superoperator acting as

$$IA = A. \qquad (5)$$

Ionization Operators' Subspace

In this work, we wish to compute perturbative corrections to the Koopmans' approximation of ionization energy [19] with the use of Eq. (2). For this reason, as the zero-order term of (3) we take the superoperator corresponding to the Fockian of the neutral molecule:

$$\mathcal{H}^0 = \mathcal{F},$$

with $\mathcal{F}$ being defined by $\mathcal{F}A = [F, A]$, similarly as for $\mathcal{H}$. The eigenvectors of $\mathcal{F}$ are easily found to be any product of second quantized creation and annihilation operators, which correspond to the molecular orbitals of the neutral system. In particular, the zero-order solution for the ionization from the ith canonical orbital is

$$\mathcal{F}|a_i) = -\epsilon_i|a_i),$$

with ϵ_i standing for the ith orbital energy. Consequently, $\omega^0 = -\epsilon_i$ and the projector O of the previous section becomes

$$O = |a_i)(a_i|$$

in our case. To proceed further, with constructing P and $\mathcal{D}^0$, we need to specify in more detail the superoperator of unity. In other words, the question arises, to what operators A in Eq. (5) should I map itself? In the present case, we need to construct I to span a sector of the Fock space that contains second quantized operator products describing single ionization processes. The operators of this kind are

$$a_p, \ a_p^\dagger a_q a_r, \ a_p^\dagger a_q^\dagger a_r a_s a_t, \ \text{etc.,} \tag{6}$$

with subscripts running over all orbital indices. For any operator like this we take the binary product most simply to be [6, 16]

$$(A|B) = \langle \Phi | [A^\dagger, B]_+ | \Phi \rangle, \tag{7}$$

where for Φ we take the Fermi vacuum corresponding to the neutral system, $|HF\rangle$. So that the product of Eq. (7) becomes a scalar product in the strict sense, one needs to exclude ionization operators from the set of (6) that have zero norm. Further, it is useful to select an orthonormal set with respect to (7) among the operators in (6). This is usually achieved by devising the following subset of (6) [6]:

$$\{a_j\} \cup \{a_b\} \cup \{a_j^\dagger a_b a_c | b > c\} \cup \{a_b^\dagger a_j a_k | j > k\}$$

$$\cup \ \{a_j^\dagger a_k^\dagger a_b a_c a_d | j > k, \ b > c > d\}$$

$$\cup \ \{a_b^\dagger a_c^\dagger a_j a_k a_l | b > c, \ j > k > l\} \cup \ldots, \tag{8}$$

where subscripts $i, j, k, l, \ldots$ run for the indices of occupied orbitals of the neutral system and $b, c, d, \ldots$ for virtuals. In what follows restriction on the occu-

pancy will rather be made by introducing occupation numbers to reduce the length of formulae. Indices p, $q, \ldots$ will then stand for any kind of orbitals.

Let us address shortly the question, why are just operators in (8) selected from the set of (6)?

1. Operators that are normal ordered with respect to $|vac\rangle$ are considered without loss of generality.
2. Index ordering is introduced to avoid trivial overcounting.
3. Index repetition among creation (annihilation) operators is excluded, for these operators are zero.
4. Index repetition between creation and annihilation operators is excluded, for the effect of these on $|HF\rangle$ is the same as the effect of a certain linear combination of operators of lower rank (the rank of a product of second quantized operators we define as the number of creation and annihilation operators that it contains).*
5. Restriction for the occupation numbers is introduced to avoid operators of zero norm, namely, because the norm of an element A that fulfills requirements (1)–(4) $A = a_p^\dagger \ldots a_q^\dagger a_r \ldots a_s$, with $p > \cdots > q$ & $r > \cdots > s$ is

$$(A|A)^{1/2}$$
$$= \sqrt{n_p \ldots n_q \bar{n}_r \ldots \bar{n}_s + \bar{n}_p \ldots \bar{n}_q n_r \ldots n_s},$$

where n_p is the occupation number of orbital p in $|HF\rangle$ and $\bar{n}_p = 1 - n_p$.

Without further studying whether or not the set (8) is a full set in the sector in which we wish to work, we consider operator I to span the space of which these elements are the basis vectors. Therefore, we take the spectral resolution of I to be

$$I = \sum_p |a_p)(a_p| + \sum_{\substack{pqr \\ (q>r)}} N_{p,qr}^+ |a_{p,qr})(a_{p,qr}|$$

$$+ \sum_{\substack{pqrst \\ (p>q, \ r>s>t)}} N_{pq,rst}^+ |a_{pq,rst})(a_{pq,rst}| + \ldots$$

with the shorthands

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*The particle rank of an operator is more conveniently defined by half of the number of creation and annihilation operators, so that, e.g., a one-electron operator has a particle rank 1. We take, however, twice this number now to avoid half ranks.

$$a_{p,qr} = a_p^\dagger a_q a_r \quad \text{and} \quad a_{pq,rst} = a_p^\dagger a_q^\dagger a_r a_s a_t$$

$$N_{p,qr}^+ = (n_p \bar{n}_q \bar{n}_r + \bar{n}_p n_q n_r) \quad \text{and}$$

$$N_{pq,rst}^+ = (n_p n_q \bar{n}_r \bar{n}_s \bar{n}_t + \bar{n}_p \bar{n}_q n_r n_s n_t).$$

PT Formulae for Single Ionization

The basis vectors that are selected to span our subspace are eigenvectors of $\mathscr{F}$, as mentioned previously; therefore, the spectral resolution of $\mathscr{F}$ and that of $\mathscr{D}^0(z)$ may also be given as

$$\mathscr{F} = \sum_p (-\epsilon_p) |a_p)(a_p|$$
$$+ \sum_{\substack{pqr \\ (q>r)}} (\epsilon_p - \epsilon_q - \epsilon_r) |a_{p,qr})(a_{p,qr}| N_{p,qr}^+ + \dots \quad (9)$$

and

$$\mathscr{D}^0(z) = \sum_{p \neq i} \frac{|a_p)(a_p|}{z + \epsilon_p}$$
$$+ \sum_{\substack{pqr \\ (q>r)}} \frac{|a_{p,qr})(a_{p,qr}|}{z - \epsilon_p + \epsilon_q + \epsilon_r} N_{p,qr}^+ + \dots, \quad (10)$$

where when getting this latter equation we used that

$$P = I - |a_i)(a_i| = \sum_{p \neq i} |a_p)(a_p|$$
$$+ \sum_{\substack{pqr \\ (q>r)}} |a_{p,qr})(a_{p,qr}| N_{p,qr}^+ + \dots.$$

Substituting Eqs. (9) and (10) into the PT correction terms of Eq. (4), one finds

$$\omega_i^{(2)} = (a_i | \mathscr{W} \mathscr{D}^0(\omega_i) \mathscr{W} | a_i)$$
$$= \sum_{\substack{pqr \\ (q>r)}} \frac{(a_i | \mathscr{W} a_{p,qr})(a_{p,qr} | \mathscr{W} a_i)}{\omega_i - \epsilon_p + \epsilon_q + \epsilon_r} N_{p,qr}^+ \quad (11)$$

for the second-order term and

$$\omega_i^{(3)} = (a_i | \mathscr{W} \mathscr{D}^0(\omega_i) \mathscr{W} \mathscr{D}^0(\omega_i) \mathscr{W} | a_i)$$
$$= \sum_{\substack{pqr \\ (q>r)}} \left[\sum_{\substack{stu \\ (t>u)}} \frac{(a_i | \mathscr{W} a_{s,tu})(a_{s,tu} | \mathscr{W} a_{p,qr})}{\omega_i - \epsilon_s + \epsilon_t + \epsilon_u} N_{s,tu}^+ \right.$$

$$+ \sum_{\substack{stuvx \\ (s>t,\, u>v>x)}} \frac{(a_i | \mathscr{W} a_{st,uvx})(a_{st,uvx} | \mathscr{W} a_{p,qr})}{\omega_i - \epsilon_s - \epsilon_t + \epsilon_u + \epsilon_v + \epsilon_x}$$

$$\left. \times N_{st,uvx}^+ \right] \frac{(a_{p,qr} | \mathscr{W} a_i)}{\omega_i - \epsilon_p + \epsilon_q + \epsilon_r} N_{p,qr}^+ \quad (12)$$

for the third-order term.

The relative simplicity of formulae (11) and (12) is due to the fact that the rank of an operator string is reduced by two upon commutation with another. Because of this, when the superoperator $\mathscr{W}$ acts on an operator it raises its rank by four—for $\mathscr{W}$ is a two-electron operator—and reduces it by two—for it forms a commutator. Therefore, after having operated with $\mathscr{W}$ the rank is increased by two altogether. This has the consequence that matrix elements like $(a_{pq,rst} | \mathscr{W} a_i)$, $(a_{pqr,stuv} | \mathscr{W} a_i)$, etc. vanish if $a_{pq,rst}$ and $a_{pqr,stuv}$ obey rules (1)–(4). For this reason, at most operators of rank 3 contribute to the second-order term, and it can be reasoned in a similar way why at most operator products of rank 5 appear at third order.

Inspecting expression (12), the non-Hermitean property of $\mathscr{W}$ with the scalar product (7) becomes apparent. The reason for the appearance of a second term on the right side of Eq. (12) is due to the fact that, $a_{pq,rst}$ fulfilling requirements (1)–(4), the matrix element $(a_i | \mathscr{W} a_{pq,rst})$ is nonzero unlike $(a_{pq,rst} | \mathscr{W} a_i)$, which is zero.

By utilizing the basic anticommutation rules, and computing expectation values with $|HF\rangle$, the second-order correction of Eq. (11) is easily shown to be identical with the ordinary second-order Dyson correction or Born collision [16, 20, 21] for the IPs.

It may also be simply verified that

$$(a_p | \mathscr{W} a_q) = 0$$

in the canonical basis; consequently, the first-order correction in Eq. (4) vanishes. The fact that

$$\omega_i = -\epsilon_i + \mathbb{O}(2)$$

may be interpreted as the formulation of Koopmans' theorem [19] in this framework.

Optimal Level Shifts for the Ionization Potential

The second-order Dyson correction to the ionization potential, Eq. (11), is known to perform poorly

[14, 15], and a great deal of effort has been put into going beyond it. The perturbative approximation can be improved in two ways: once by stepping to the next term in the series or at least computing certain terms of the third order [22, 23]. Alternatively, or at the same time the convergence of the series may be graded up by incorporating some correlation effect in the reference function $|\Phi\rangle$ in Eq. (7) or even taking a different expression for the binary product [24–27]. Level shifts have also been used to affect the convergence and consequently alter the performance of low-order approximations [21].

Another way to step beyond Eq. (11) is to apply a strategy different from a simple PT (e.g., Green's functions techniques, which use nondiagonal approximation of the self-energy matrix, fall into this category [15, 26–28]).

The purpose of this article is to investigate whether a simple level shift of the form

$$\mathcal{H}^{0'} = \mathcal{F} - \sum_{\substack{pqr \\ (q>r)}} \lambda_{p,qr} |a_{p,qr})(a_{p,qr}| N^+_{p,qr}$$

$$\mathcal{W}' = \mathcal{W} + \sum_{\substack{pqr \\ (q>r)}} \lambda_{p,qr} |a_{p,qr})(a_{p,qr}| N^+_{p,qr}$$

can help to get the second-order result better. Previously [9], applying Rayleigh–Schödinger (RS) PT for correlation energies we found that a modification like this does improve the convergence of the series, as well as low-order approximations, if the shift parameters are chosen in a way that the third-order RS correction (i.e., substituting $-\epsilon_i$ for ω_i in our case) vanishes term by term in the new partitioning. The resulting partitioning is addressed as "optimal" for it can be shown that this criterion arises from an almost variational condition for the first-order wave function in the shifted partitioning [9]. Rewriting Eq. (12) for the new partitioning, and equating it zero term by term, one is led to

$$\sum_{\substack{stu \\ (t>u)}} \frac{(a_i|\mathcal{W}a_{s,tu})(a_{s,tu}|\mathcal{W}'a_{p,qr})}{-\epsilon_i - \epsilon_s + \epsilon_t + \epsilon_u + \lambda_{s,tu}} N^+_{s,tu}$$

$$+ \sum_{\substack{stuvx \\ (s>t,\, u>v>x)}} \frac{(a_i|\mathcal{W}a_{st,uvx})(a_{st,uvx}|\mathcal{W}a_{p,qr})}{-\epsilon_i - \epsilon_s - \epsilon_t + \epsilon_u + \epsilon_v + \epsilon_x} N^+_{st,uvx} = 0$$

$$(13)$$

for each pqr, $q > r$, $((p \in occ) \wedge (q, r \in virt)) \vee ((p \in virt) \wedge (q, r \in occ))$. Condition (13) is a linear inhomogeneous system of equations for $1/(\Delta^{is}_{tu} +$

$\lambda_{s,tu})$ with $\Delta^{is}_{tu} = -\epsilon_i - \epsilon_s + \epsilon_t + \epsilon_u$, which can be seen by rearranging Eq. (13) to the form

$$\sum_{\substack{stu \\ (t>u)}} \left[\delta_{sp}\delta_{tq}\delta_{ur}\Delta^{ip}_{qr} - \frac{(a_i|\mathcal{W}a_{s,tu})(a_{s,tu}\mathcal{W}a_{p,qr})}{(a_i|\mathcal{W}a_{p,qr})} \right]$$

$$\times N^+_{s,tu} \frac{1}{\Delta^{is}_{tu} + \lambda_{s,tu}} = N^+_{p,qr}$$

$$+ \sum_{\substack{stuvx \\ (s>t,\, u>v>x)}} \frac{(a_i|\mathcal{W}a_{st,uvx})(a_{st,uvx}|\mathcal{W}a_{p,qr})}{(a_i|\mathcal{W}a_{p,qr})}$$

$$\times \frac{1}{(-\epsilon_i - \epsilon_s - \epsilon_t + \epsilon_u + \epsilon_v + \epsilon_x)} N^+_{st,uvx}. \quad (14)$$

In our implementation so far we have neglected the terms arising from operators of rank 5 when determining the shift parameters, that is, our working equation for computing $\lambda_{s,tu}$s is simplified to

$$\sum_{\substack{stu \\ (t>u)}} \left[\delta_{sp}\delta_{tq}\delta_{ur}\Delta^{ip}_{qr} - \frac{(a_i|\mathcal{W}a_{s,tu})(a_{s,tu}\mathcal{W}a_{p,qr})}{(a_i|\mathcal{W}a_{p,qr})} \right]$$

$$\times N^+_{s,tu} \frac{1}{\Delta^{is}_{tu} + \lambda_{s,tu}} = N^+_{p,qr}. \quad (15)$$

The level shifts of the so-called shifted Born collision approximation [21] can be derived, further simplifying Eq. (15) by ignoring the off-diagonal matrix elements of $\mathcal{W}$ of the type $(a_{s,tu}|\mathcal{W}a_{p,qr})$ if $(s \neq p) \vee (t \neq q) \vee (u \neq r)$. Like this the level shifts become simply

$$\lambda_{p,qr} = -(a_{p,qr}|\mathcal{W}a_{p,qr}), \quad (16)$$

which leads to the Epstein–Nesbet partitioning in this framework.

Note that level shifts defined by criteria (13) or (14) depend on index i. This means that to each ionization potential there is a different set of level shift parameters that set the third-order correction to zero.

Solution of Eq. (15) for λ-s requires either an explicit inversion of the coefficient matrix or a suitable iteration procedure. According to our experience, convergence properties of such an iteration are usually satisfactory. In case of convergence problems, it is preferable to collect dominant elements of the coefficient matrix into one block that should be inverted explicitly before starting with iterations.

TABLE I

First ionization potentials (a.u.) for the H_2O molecule, at geometry $R_{OH} = 0.96$ Å, $\angle(H, O, H) = 105°$ and for the N_2 molecule, the bond length being $R = 1.1$ Å.

Basis	EOMIP	Koopmans	DY2	SBC	~OPTDY2
H_2O molecule					
STO-3G	0.308	0.391	0.303	0.282	0.299
6-31G	0.427	0.501	0.398	0.387	0.417
6-311G**	0.442	0.499	0.410	0.404	0.429
N_2 molecule					
6-31G	0.544	0.629	0.529	0.498	0.545
6-31G**	0.562	0.630	0.545	0.522	0.557

Koopmans' values and perturbative approximations, such as second-order Dyson correction (DY2), SBC, and shifted second-order Dyson correction with shifts got from Eq. (15) (~OPTDY2) are tabulated. The so-called EOMIP results, got with using the CCSD wave function, are given for comparison.

Also, it may be worth noting that a single-electron attachment can be dealt with in a similar manner. Carrying out the derivation one is led to just the same structure for the PT corrections as Eqs. (11) and (12) with signs reversed. The same holds for the PT terms of the level shifted partitioning if shift parameters are introduced with proper signs. For the interested reader, formulae for electron attachment are collected in the Appendix.

Having determined the value of the shifts from Eqs. (16) or (15) we are interested in how the second-order PT correction in the shifted partitioning

$$\omega_i^{(2)'} = \sum_{\substack{pqr \\ (q>r)}} \frac{(a_i|\mathcal{W}a_{p,qr})(a_{p,qr}|\mathcal{W}a_i)}{\omega_i - \epsilon_p + \epsilon_q + \epsilon_r + \lambda_{p,qr}} N_{p,qr}^+ \qquad (17)$$

behaves if compared to the unshifted formula (11). A few preliminary examples for this are given in the following section.

Application

A limited amount of examples are presented in this section for the effect of level shift parameters when computing the second-order Dyson correction to Koopmans' ionization potentials. The aim with getting these few numbers were two-fold: first, to investigate whether the earlier elaborated determination of level shifts performs similarly well if applied for IPs as it does for the correlation energy; second, to have an impression of whether it may be worth using Eq. (14) instead of the simplified Eq. (15) to set the value of the shift parameters. Clearly, the third-order correction vanishes in the new partitioning only if Eq. (14) is used, but Eq. (15) is considerably cheaper to fulfill.

Several perturbative approximations to the lowest IP of the water and nitrogen molecules are shown in Table I. For comparison, the relatively costly but more accurate EOMIP results are also given [29–31], computed using a CCSD wave function. The PT corrections are computed from Eq. (17), iterating the expression for ω_i. Level shifts are taken from Eq. (16) in the case of the shifted Born collision (SBC) and from Eq. (15) for ~OPTDY2. Unshifted results are got iterating Eq. (11) for ω_i; these are denoted by DY2 in Table I. Comparing the zeroth- and second-order PT results with the EOMIP figures, one sees that DY2 significantly improves the Koopmans' approximation but still has an error in the second significant digit. The shifted Born collision approximation worsens DY2 in each case tabulated. If the simplified form of the optimal condition for the shift parameters, Eq. (15), is used, the DY2 values are improved in all cases shown except for the minimal basis result for H_2O, where the DY2 correction is already accurate. Typical differences between ~OPTDY2 and EOM-IP results are merely a few tenths of an electron volt, the partial optimization reducing the error of the DY2 results by about 70% on average. We cannot claim, however, that ~OPTDY2 performs so well in other cases. Work in our laboratory is in progress toward studying whether levels shifts got from Eq. (14) have a similar but amplified effect on the second-order PT correction.

Appendix: PT Formulae for Electron Attachment

$$a^\dagger_{qr,p} = a^\dagger_q a^\dagger_r a_p \quad \text{and} \quad a^\dagger_{rst,pq} = a^\dagger_r a^\dagger_s a^\dagger_t a_p a_q$$

$$N^+_{qr,p} = (n_q n_r \bar{n}_p + \bar{n}_q \bar{n}_r n_p) \quad \text{and}$$

$$N^+_{rst,pq} = (n_r n_s n_t \bar{n}_p \bar{n}_q + \bar{n}_r \bar{n}_s \bar{n}_t n_p n_q)$$

$$I = \sum_p |a^\dagger_p)(a^\dagger_p| + \sum_{\substack{pqr \\ (q>r)}} N^+_{qr,p} |a^\dagger_{qr,p})(a^\dagger_{qr,p}|$$

$$+ \sum_{\substack{pqrst \\ (r>s>t,p>q)}} N^+_{rst,pq} |a^\dagger_{rst,pq})(a^\dagger_{rst,pq}| + \ldots$$

$$\mathcal{H} = \mathcal{F} + \mathcal{W}$$

$$\mathcal{F}|a^\dagger_b) = \epsilon_b |a^\dagger_b); \quad O = |a^\dagger_b)(a^\dagger_b|; \quad P = I - |a^\dagger_b)(a^\dagger_b|$$

$$\mathcal{Q}^0(z) = \sum_{p \neq b} \frac{|a^\dagger_p)(a^\dagger_p|}{z - \epsilon_p}$$

$$+ \sum_{\substack{pqr \\ (q>r)}} \frac{|a^\dagger_{qr,p})(a^\dagger_{qr,p}|}{z + \epsilon_p - \epsilon_q - \epsilon_r} N^+_{qr,p} + \ldots$$

$$\omega_b = \epsilon_b + (a^\dagger_b|\mathcal{W}|a^\dagger_b) + (a^\dagger_b|\mathcal{W}\mathcal{Q}^0(\omega_b)\mathcal{W}|a^\dagger_b)$$

$$+ (a^\dagger_b|\mathcal{W}\mathcal{Q}^0(\omega_b)\mathcal{W}\mathcal{Q}^0(\omega_b)\mathcal{W}|a^\dagger_b) + \ldots$$

$$\omega_b^{(2)} = \sum_{\substack{pqr \\ (q>r)}} \frac{(a^\dagger_b|\mathcal{W}a^\dagger_{qr,p})(a^\dagger_{qr,p}|\mathcal{W}a^\dagger_b)}{\omega_b + \epsilon_p - \epsilon_q - \epsilon_r} N^+_{qr,p}. \tag{A1}$$

$$\omega_b^{(3)} = \sum_{\substack{pqr \\ (q>r)}} \left[\sum_{\substack{stu \\ (t>u)}} \frac{(a^\dagger_b|\mathcal{W}a^\dagger_{tu,s})(a^\dagger_{tu,s}|\mathcal{W}a^\dagger_{qr,p})}{\omega_b + \epsilon_s - \epsilon_t - \epsilon_u} N^+_{tu,s} \right.$$

$$+ \sum_{\substack{stuvx \\ (u>v>x, s>t)}} \frac{(a^\dagger_b|\mathcal{W}a^\dagger_{uvx,st})(a^\dagger_{uvx,st}|\mathcal{W}a^\dagger_{qr,p})}{\omega_b + \epsilon_s + \epsilon_t - \epsilon_u - \epsilon_v - \epsilon_x}$$

$$\left. \times N^+_{uvx,st} \right] \frac{(a^\dagger_{qr,p}|\mathcal{W}a^\dagger_b)}{\omega_b + \epsilon_p - \epsilon_q - \epsilon_r} N^+_{qr,p}. \tag{A2}$$

$$\mathcal{H} = \mathcal{H}^{0'} + \mathcal{W}'$$

$$\mathcal{H}^{0'} = \mathcal{F} + \sum_{\substack{pqr \\ (q>r)}} \lambda_{qr,p} |a^\dagger_{qr,p})(a^\dagger_{qr,p}| N^+_{pq,r}$$

$$\mathcal{W}' = \mathcal{W} - \sum_{\substack{pqr \\ (q>r)}} \lambda_{qr,p} |a^\dagger_{qr,p})(a^\dagger_{qr,p}| N^+_{qr,p}$$

$$\omega_b^{(2)'} = \sum_{\substack{pqr \\ (q>r)}} \frac{(a^\dagger_b|\mathcal{W}a^\dagger_{qr,p})(a^\dagger_{qr,p}|\mathcal{W}a^\dagger_b)}{\omega_b + \epsilon_p - \epsilon_q - \epsilon_r - \lambda_{qr,p}} N^+_{qr,p}.$$

$$\tag{A3}$$

$$\omega_b^{(3)'} = \sum_{\substack{pqr \\ (q>r)}} \left[\sum_{\substack{stu \\ (t>u)}} \frac{(a^\dagger_b|\mathcal{W}a^\dagger_{tu,s})(a^\dagger_{tu,s}|\mathcal{W}a^\dagger_{qr,p})}{\omega_b + \epsilon_s - \epsilon_t - \epsilon_u - \lambda_{tu,s}} N^+_{tu,s} \right.$$

$$+ \sum_{\substack{stuvx \\ (u>v>x, s>t)}} \frac{(a^\dagger_b|\mathcal{W}a^\dagger_{uvx,st})(a^\dagger_{uvx,st}|\mathcal{W}a^\dagger_{qr,p})}{\omega_b + \epsilon_s + \epsilon_t - \epsilon_u - \epsilon_v - \epsilon_x}$$

$$\left. \times N^+_{uvx,st} \right] \frac{(a^\dagger_{qr,p}|\mathcal{W}a^\dagger_b)}{\omega_b + \epsilon_p - \epsilon_q - \epsilon_r - \lambda_{qr,p}} N^+_{qr,p}.$$

$$\sum_{\substack{stu \\ (t>u)}} \left[\delta_{sp}\delta_{tq}\delta_{ur}\Delta^{qr}_{bp} - \frac{(a^\dagger_b|\mathcal{W}a^\dagger_{tu,s})(a^\dagger_{tu,s}|\mathcal{W}a^\dagger_{qr,p})}{(a^\dagger_b|\mathcal{W}a^\dagger_{qr,p})} \right]$$

$$\times N^+_{tu,s} \frac{1}{\Delta^{tu}_{bs} - \lambda_{tu,s}} = N^+_{qr,p}$$

$$+ \sum_{\substack{stuvx \\ (u>v>x, s>t)}} \frac{(a^\dagger_b|\mathcal{W}a^\dagger_{uvx,st})(a^\dagger_{uvx,st}|\mathcal{W}a^\dagger_{qr,p})}{(a^\dagger_b|\mathcal{W}a^\dagger_{qr,p})}$$

$$\times \frac{1}{(\epsilon_b + \epsilon_s + \epsilon_t - \epsilon_u - \epsilon_v - \epsilon_x)} N^+_{uvx,st}. \tag{A4}$$

Differences between formulae (11) and (A1), (12) and (A2), (14) and (A4), and (17) and (A3) appear only in the signs as

$$(a^\dagger_s|\mathcal{W}a^\dagger_{qr,p}) N^+_{qr,p} = (a_s|\mathcal{W}a_{p,qr}) N^+_{p,qr}$$

$$(a^\dagger_{qr,p}|\mathcal{W}a^\dagger_s) N^+_{qr,p} = (a_{p,qr}|\mathcal{W}a_s) N^+_{p,qr}$$

$$(a^\dagger_{tu,s}|\mathcal{W}a^\dagger_{qr,p}) N^+_{qr,p} N^+_{tu,s} = -(a_{s,tu}|\mathcal{W}a_{p,qr}) N^+_{p,qr} N^+_{s,tu}$$

$$(a^\dagger_p|\mathcal{W}a^\dagger_{uvx,st}) N^+_{uvx,st} = -(a_p|\mathcal{W}a_{st,uvx}) N^+_{st,uvx}$$

$$(a^\dagger_{qr,p}|\mathcal{W}a^\dagger_{uvx,st}) N^+_{qr,p} N^+_{uvx,st} = (a_{p,qr}|\mathcal{W}a_{st,uvx}) N^+_{p,qr} N^+_{st,uvx}.$$

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