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Post-Wick theorems for symbolic manipulation of second-quantized expressions in atomic many-body perturbation theory

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Abstract

Manipulating expressions in many-body perturbation theory becomes unwieldy with increasing order of the perturbation theory. Here I derive a set of theorems for efficient simplification of such expressions. The derived rules are specifically designed for implementing with symbolic algebra tools. As an illustration, we count the numbers of Brueckner–Goldstone diagrams in the first several orders of many-body perturbation theory for matrix elements between two states of a mono-valent system.

Many-body perturbation theory (MBPT) has proven to be a powerful tool in physics [1] and quantum chemistry [2]. Although MBPT provides a systematic approach to solving the many-body problem, the number and complexity of analytical expressions becomes rapidly unwieldy with increasing order of perturbation theory. At the same time, exploring higher orders is desirable for improving accuracy of *ab initio* atomic-structure methods. Here, a number of applications may benefit, ranging from atomic parity violation [3] and atomic clocks [4, 5] to a precision characterization of long-range inter-atomic potentials for ultra-cold collision studies [6].

To overcome an overwhelming complexity of the MBPT in high orders, one has to develop symbolic tools that automate highly repetitive but error-prone derivation of many-body diagrams. The advantage of using symbolic algebra computing for these goals has been realized for a number of decades. For example, the pioneering ‘Schoonschip’ program [7] and other symbolic packages are employed for evaluating Feynman diagrams in quantum electrodynamics and high-energy physics. We also note similar efforts in quantum chemistry [8] (see also [9] and references therein). In atomic MBPT, developing symbolic tools was reported by the Notre Dame [10], Michigan [11], and very recently by the Sydney [12] and Kassel groups [13].

In practical applications of MBPT, one deals with products of strings of creation and annihilation operators. Typically such products are evaluated with Wick’s theorem (see, e.g.

discussion in [14]). This is the point of departure of the symbolic calculations described in [10] and [11]. The application of Wick’s theorem results in a series of Kronecker delta symbols. The next step in the derivation requires carrying out summation over the delta symbols. In a typical application, the resulting terms are redundant and require additional efforts to further simplify and combine the expressions. The complexity of both the application of Wick’s theorem and the further simplification grows rapidly as the order of perturbation theory increases.

Over the past decade, our group in Reno has developed an alternative set of symbolic tools for MBPT. The goal of our work was to study high orders of MBPT, e.g. fourth-order contributions to matrix elements for mono-valent atoms [15, 16]. In our practical work, we found that the conventional approaches based on the straightforward applications of Wick’s theorem require prohibitively long computational times. To overcome this difficulty, I have derived a set of rules enabling efficient derivation of MBPT expressions for fermionic systems in high orders of MBPT. These theorems are reported here.

Wick’s theorem works at the level of elemental pairwise contractions of creation and annihilation operators. The basic idea of the present approach is to shortcut directly to the resulting expressions for typical operations in MBPT, without the need to apply expensive pairwise operations. The theorems are formulated as a set of symbolic replacement

rules, ideally suited for implementing with symbolic algebra systems. We provide an accompanying Mathematica package downloadable from the author's website [17]. In this work, we focus on mono-valent systems.

The paper is organized as follows. In section 1, we review main results from the many-body perturbation theory and introduce notation. In sections 2.1 and 2.3, we derive rules for multiplying second-quantized operators with atomic wavefunctions. Similar theorems are derived for determining MBPT corrections to energies and matrix elements in section 3. Finally, as an illustration, in section 4 we derive explicit expressions for matrix elements in several first orders of MBPT and count the number of resulting diagrams.

1. Background and notation

1.1. Second quantization, normal forms and Wick's theorems

We start by recapitulating relevant notation and results from the second-quantization method as applied to fermionic systems.

At the heart of the second quantization technique lies an expansion of the true many-body wave function over properly anti-symmetrized products of single-particle orbitals (the Slater determinants). The machinery is simplified by introducing the creation (a_k^\dagger) and the annihilation (a_k) operators satisfying the anti-commutation relations

$$\begin{aligned} a_j^\dagger a_k^\dagger &= -a_k^\dagger a_j^\dagger, & a_j a_k &= -a_k a_j, \\ a_j a_k^\dagger &= \delta_{jk} - a_k^\dagger a_j, & a_j a_j &\equiv 0, & a_j^\dagger a_j^\dagger &\equiv 0. \end{aligned}$$

Applying strings of creation and annihilation operators to the vacuum state $|0\rangle$ builds the Slater determinants. A one-particle operator in the second quantization (such as an interaction with an external field) reads

$$Z = \sum_{kl} z_{kl} a_k^\dagger a_l. \quad (1)$$

A two-particle operator (such as a pairwise Coulomb interaction between electrons) is represented as

$$G = \frac{1}{2} \sum_{ijkl} g_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \quad (2)$$

$$= \frac{1}{4} \sum_{ijkl} \tilde{g}_{ijkl} a_i^\dagger a_j^\dagger a_l a_k. \quad (3)$$

Matrix elements z_{kl} and g_{ijkl} are conventionally defined on the basis of single-particle orbitals. Symmetry of the two-particle operator with respect to permuting electron labels leads to $g_{ijkl} = g_{jilk}$. By renaming summation indices in equation (2) and using anti-commutation rules, we may express G in terms of the anti-symmetrized combination $\tilde{g}_{ijkl} = g_{ijkl} - g_{jilk}$, equation (3). Apparently, swapping indices leads to the following properties,

$$\tilde{g}_{ijkl} = -\tilde{g}_{ijlk} = -\tilde{g}_{jikl} = \tilde{g}_{jilk}. \quad (4)$$

Conventionally, in applications of the second quantization technique to many-electron systems, one distinguishes between three groups of single-particle states (orbitals): core, virtual (excited) and valence orbitals. The core orbitals are

occupied and form the quasi-vacuum state $|0_c\rangle$. Virtual orbitals are unoccupied in $|0_c\rangle$. We will treat valence orbitals as a part of the set of virtual orbitals. We follow a convention of [14] and label core orbitals as a, b, \dots , excited (virtual) orbitals as m, n, \dots , and valence orbitals as v, w . Indexes i, j, k, l run over both core and virtual orbitals. For example, in the independent-particle-approximation, a state of a mono-valent atom may be represented as $a_v^\dagger |0_c\rangle$, where the quasi-vacuum state $|0_c\rangle = (\prod_{a \in \text{core}} a_a^\dagger) |0\rangle$ represents a closed-shell atomic core.

Further, we review several results related to the normal form of operator products, $:\dots:$. The operators are rearranged so that a_{core} and a_{virt}^\dagger appear to the left of a_{core}^\dagger and a_{virt} . When acted on the $|0_c\rangle$ quasi-vacuum state, most of the strings of operators in the normal form produce vanishing result.

One of the central results related to the normal forms is Wick's expansion into normal products

$$A = :A: + : \bar{A} :,$$

$:\bar{A}:$ being a sum of normal ordered terms obtained by making all possible single, double, triple, \dots contractions within A . Contractions between two creation/annihilation operators x and y are defined as $\overline{xy} \equiv xy - :xy:$. The overall sign of $:A:$ is $(-1)^p$, p being a number of permutations to bring A into the normal form. The same rule holds for terms in $:\bar{A}:$ —we count permutations necessary to bring the operators being contracted next to each other and also the permutations needed to arrange the resulting term in the normal form. The only nonvanishing contractions are

$$\overline{a_m a_n^\dagger} = \delta_{mn}, \quad \overline{a_a^\dagger a_b} = \delta_{ab}.$$

All contractions between the core and excited (including valence) orbitals vanish.

Using Wick's expansion, one can rewrite a single-particle operator Z , equation (1), as a sum of zero-body (scalar) and one-body contributions [14]

$$\begin{aligned} Z &= Z_0 + Z_1, \\ Z_0 &= \sum_a z_{aa} \\ Z_1 &= \sum_{ij} z_{ij} : a_i^\dagger a_j :. \end{aligned} \quad (5)$$

Similarly, any two-particle operator G , equation (2), may be represented as a sum of zero-body $G^{(0)}$, one-body $G^{(1)}$ and two-body $G^{(2)}$ terms,

$$\begin{aligned} G &= G_0 + G_1 + G_2, \\ G_0 &= \frac{1}{2} \sum_{ab} \tilde{g}_{abab}, \\ G_1 &= \sum_{ij} \left(\sum_a \tilde{b}_{iaja} \right) : a_i^\dagger a_j :, \\ G_2 &= \frac{1}{4} \sum_{ijkl} \tilde{b}_{ijkl} : a_i^\dagger a_j^\dagger a_l a_k :. \end{aligned} \quad (6)$$

Technically, the MBPT formalism requires multiplying second-quantized operators. Simplification of the resulting

expressions is greatly aided by Wick's theorem for operator products. For two strings of operators in the normal form : A : and : B :, the theorem states

$$: A :: B :=: AB : + : \overline{AB} : . \quad (7)$$

Here : \overline{AB} : represents the sum of the normal-ordered terms with all possible contractions between the operators in A and those in B .

1.2. MBPT for mono-valent atoms

To gain insight into a general structure of MBPT expressions, here we briefly reiterate MBPT formalism [15] for atoms with a single valence electron outside a closed-shell core. The lowest order valence wavefunction is simply $|\Psi_v^{(0)}\rangle = a_v^\dagger|0_c\rangle$, where v is a valence orbital. The perturbation expansion is built in powers of the residual interaction V_I defined as a difference between the full Coulomb interaction between the electrons and the model potential used to generate the single-particle basis. The n th-order correction to the valence wavefunction may be expressed as

$$|\Psi_v^{(n)}\rangle = -R_v \{ Q V_I |\Psi_v^{(n-1)}\rangle \}_{\text{linked}}, \quad (8)$$

where R_v is a resolvent operator modified to include so-called folded diagrams [15], projection operator $Q = 1 - |\Psi_v^{(0)}\rangle\langle\Psi_v^{(0)}|$ and only linked diagrams [14] are to be kept. For mono-valent systems, a convenient starting point is a single-particle basis generated in the frozen-core (V^{N-1}) Hartree-Fock (HF) approximation [18]. In this approximation, the residual interaction is simplified to a two-body part, G_2 , of the Coulomb interaction and the number of MBPT diagrams is substantially reduced [10, 14].

The recursion relation, equation (8), systematically solves the many-body problem, as we may generate corrections to the wavefunction at any given order of the perturbation theory. With such calculated corrections to wavefunctions of two valence states w and v , the n th-order contribution to matrix elements of an operator \hat{Z} may be determined as

$$Z_{wv}^{(n)} = \sum_{k=0}^{n-1} \langle \Psi_w^{(n-k-1)} | Z | \Psi_v^{(k)} \rangle_{\text{val,conn}} + Z_{wv,\text{norm}}^{(n)}. \quad (9)$$

Here $Z_{wv,\text{norm}}^{(n)}$ is a normalization correction arising due to an intermediate normalization scheme employed in derivation of equation (8). Subscript 'val, conn' indicates that only connected diagrams involving excitations from valence orbitals are included in the expansion.

1.3. Generic contribution to wavefunction

Now we would like to introduce short-hand notation for strings of creation (a_k^\dagger) and annihilation (a_k) operators in the Fermi statistics. A string of x operators

$$E_\alpha^\dagger = a_1^\dagger a_2^\dagger \cdots a_x^\dagger$$

combines creation operators for excited orbitals and symbol α ranges over the set $1, 2, \dots, x$. Similarly,

$$C_\beta = a_1 a_2 \cdots a_y$$

represents a string of y annihilation operators for core orbitals, with symbol β spanning the indices $1, 2, \dots, y$. Finally, V^\dagger is either a_v^\dagger or 1 depending on the presence of the valence creation operator.

On very general grounds, a generic piece of atomic wavefunction for a mono-valent atom may be represented as

$$|\Phi\rangle = \sum_{\{\alpha\},\{\beta\}} L[(1, 2, \dots, x)_\alpha, (1, 2, \dots, y)_\beta] E_\alpha^\dagger C_\beta V^\dagger |0_c\rangle, \quad (10)$$

where $\sum_{\{\alpha\}} = \sum_1 \cdots \sum_x$, and $L[(1, 2, \dots, x)_\alpha, (1, 2, \dots, y)_\beta]$ is a c-number object which depends on the indices.

As an illustration, a doubly-excited core state of a mono-valent atom may read $\sum_{mnab} \rho_{mnab} a_m^\dagger a_n^\dagger a_a a_b a_v^\dagger |0_c\rangle$. Apparently, $x = y = 2$, $E_\alpha^\dagger = a_m^\dagger a_n^\dagger$, $C_\beta = a_a a_b$, $V^\dagger = a_v^\dagger$ and the groups of indices are $(1, 2, \dots, x)_\alpha = (m, n)$ and $(1, 2, \dots, y)_\beta = (a, b)$. In summations, the symbolic index α would run over symbols m and n (which range over all excited orbitals). Similarly, the symbolic index β assumes symbolic values a and b , i.e. the labels of the core orbitals.

The equation (10) will be the central object in our derivations presented below. We will act on this 'generic piece of wavefunction' with one- and two-body operators and also bring the resulting expressions into the very same form of equation (10).

2. Simplification theorems

We would like to follow the MBPT prescription (8) and compute the wavefunction in an arbitrary order. To this end, we will derive rules for simplifying products of one- and two-particle operators with the generic wavefunction $|\Phi\rangle$, equation (10). The wavefunction $|\Phi\rangle$ is in the normal form with respect to the quasi-vacuum state. Therefore, we take the second-quantized operators expanded in the normal forms, equations (5), (6), and apply Wick's theorem (7). Apparently, the zero-body terms Z_0 and G_0 (c-numbers) do not produce non-trivial results and in the derivation below we focus on contractions of one- and two-body operators with strings of operators entering $|\Phi\rangle$. Finally, we bring the resulting chain of operators in the same standardized sequence of operators $E_\alpha^\dagger C_\beta V^\dagger$, as in (10); of course the number of operators in each group may differ from the starting numbers of operators in $|\Phi\rangle$.

2.1. Product with a one-body operator

Here we focus on acting with the operator

$$Z_1 = \sum_{ij} z(i, j) : a_i^\dagger a_j : \quad (11)$$

on a generic wavefunction $|\Phi\rangle$, equation (10). According to Wick's theorem, we may have 0, 1 and 2 contractions between Z_1 and operators entering $|\Phi\rangle$. There are only six distinct possibilities classified by the number and type of contractions

$$\{Z_1|\Phi\rangle\} = \{Z_1|\Phi\rangle\}_0 + \{Z_1|\Phi\rangle\}_{1e} + \{Z_1|\Phi\rangle\}_{1c} + \{Z_1|\Phi\rangle\}_{1v} \\ + \{Z_1|\Phi\rangle\}_{1e,1c} + \{Z_1|\Phi\rangle\}_{1v,1c}.$$

The first term corresponds to no contractions. The term $1e$ results from contracting one excited orbital from Z_1 and one orbital from the string E_α^\dagger of the operators entering $|\Phi\rangle$. Subscript $1v, 1c$ labels double contraction: one contraction $1v$ involves an operator from the valence string V^\dagger and the other contraction $1c$ involves an operator from the core string C_β . The labeling scheme for other contributions follows from these examples.

Note that a straightforward application of the Wick theorem (7) is inefficient. Operators resulting from expanding equation (7) ultimately act on $|0_c\rangle$ and many terms in Wick's expansion will produce zero result. Indeed, we may write explicitly

$$Z_1 = \sum_{mn} z(m, n) a_m^\dagger a_n + \sum_{ma} z(a, m) a_a^\dagger a_m - \sum_{ab} z(a, b) a_b a_a^\dagger + \sum_{ma} z(m, a) a_m^\dagger a_a.$$

As an example, consider term with no contractions. Only the last contribution from the above expansion will contribute, because the first two terms annihilate an unfilled orbital in $|0_c\rangle$ and the third term promotes an electron into already occupied core orbital. Based on this discussion, we shortcut the application of the Wick theorem and limit ourselves to a much smaller subset of terms.

2.1.1. No contractions. In this case, the relevant part of the operator Z_1 contains one core annihilation operator and one creation operator involving an excited orbital. Then, we may simply move the operators from Z_1 to the ends of the excited E_α^\dagger and core C_β operator strings in the wave-function. The additional core and excited orbital indices are absorbed in the summation:

$$\{Z_1|\Phi\}_0 = \sum_{\{\alpha\},\{\beta\}} L^0[(1, 2 \dots x, x+1)_\alpha, (1, 2 \dots y, y+1)_\beta] \times (E_\alpha^\dagger a_{x+1}^\dagger)(C_\beta a_{y+1}) V^\dagger |0_c\rangle,$$

where

$$L^0[(1, 2 \dots x, x+1)_\alpha, (1, 2 \dots y, y+1)_\beta] = (-1)^y z(x+1, y+1) L[(1, 2 \dots x)_\alpha, (1, 2 \dots y)_\beta].$$

Moving a pair of operators together does not produce a phase. The phase factor appears because the excited orbital operator was additionally moved through (anti-commuted with) y operators in the C_β string.

2.1.2. Single contraction with the creation operator in the E_α^\dagger group: $1e$. There are x such contractions ($\overline{a_j a_\alpha^\dagger} = \delta_{j\alpha}$); we contract the operators in turn. By contracting with a_1^\dagger , we obtain a string of operators $a_2^\dagger \dots a_x^\dagger$ and we bring the a_i^\dagger to the end of this string thus acquiring a phase $(-1)^{x-1}$. By renaming the dummy summation indices, we may bring the resulting sequence of operators to the same form $a_2^\dagger \dots a_x^\dagger a_i^\dagger$. For example, as a result of contracting with a_μ^\dagger , we obtain

$$\delta_{j\mu} (-1)^{\mu-1} (-1)^{x-1} a_1^\dagger a_2^\dagger \dots a_{\mu-1}^\dagger a_{\mu-1}^\dagger a_x^\dagger a_i^\dagger.$$

Now we rename ($\mu \longleftrightarrow 1$) and bring the resulting string into the form $a_2^\dagger \dots a_x^\dagger a_i^\dagger$

$$\begin{aligned} \delta_{j1} (-1)^{\mu-1} (-1)^{x-1} a_\mu^\dagger a_2^\dagger \dots a_{\mu-1}^\dagger a_{\mu-1}^\dagger a_x^\dagger a_i^\dagger \\ = \delta_{j1} (-1)^{\mu-1} (-1)^{x-1} (-1)^\mu a_2^\dagger \dots a_{\mu-1}^\dagger a_\mu^\dagger a_{\mu-1}^\dagger a_x^\dagger a_i^\dagger \\ = -\delta_{j1} (-1)^{x-1} a_2^\dagger \dots a_{\mu-1}^\dagger a_\mu^\dagger a_{\mu-1}^\dagger a_x^\dagger a_i^\dagger. \end{aligned}$$

Finally,

$$\begin{aligned} \{Z|\Phi\}_{1e} &= \sum_{\{\alpha\},\{\beta\}} L^{1e}[(2 \dots x, x+1)_\alpha, (1 \dots y)_\beta] \\ &\times (a_2^\dagger \dots a_x^\dagger a_{x+1}^\dagger)_\alpha C_\beta V^\dagger |0_c\rangle, \end{aligned}$$

with

$$\begin{aligned} L^{1e}[(2 \dots x, x+1)_\alpha, (1, 2 \dots y)_\beta] &= (-1)^{x-1} \\ &\times \sum_{1_e} z(x+1, 1_e) \mathcal{A}_{1_e} L[(1_e, 2 \dots x)_\alpha, (1, \dots y)_\beta], \end{aligned}$$

where the operator \mathcal{A}_{1_e} anti-symmetrizes L over the first excited index, i.e.

$$\begin{aligned} \mathcal{A}_{1_e} L[(1_e, 2 \dots x)_\alpha, (0)_\beta] \\ = L[(1_e, 2 \dots x)_\alpha, (0)_\beta] - L[(2, 1_e, 3, \dots x)_\alpha, (0)_\beta] \\ - L[(3, 2, 1_e, \dots x)_\alpha, (0)_\beta] - \dots \end{aligned} \quad (12)$$

or

$$\mathcal{A}_{1_e} f(1, 2 \dots x) = f(1, 2 \dots x) - \sum_{\mu \neq i} f(1, 2 \dots \mu, \dots x)_{\mu \leftrightarrow i}. \quad (13)$$

As an example,

$$\mathcal{A}_{1_e} \rho_{mn,ab} = \rho_{mn,ab} - \rho_{nm,ab}.$$

Computationally, in symbolic algebra implementations, the symbol replacement operations in equation (13) are efficient. We note that $\mathcal{A}_{1_e} \tilde{L} = x \tilde{L}$.

2.1.3. Single contraction with the annihilation operator in the C_β group: $1c$. The derivation is similar to the previous case; $a_i^\dagger a_\beta = \delta_{i\beta}$. There is a phase factor $(-1)^{x+y}$ due to the transfer of a_j through $E_\alpha^\dagger C_\beta$ and an additional factor $(-1)^x$ due to moving the a_i^\dagger to the beginning of the C_β group, resulting in the total phase of $(-1)^y$. The result reads

$$\begin{aligned} \{Z|\Phi\}_{1c} &= \sum_{\{\alpha\},\{\beta\}} L^{1c}[(1 \dots x)_\alpha, (2 \dots y, y+1)_\beta] \\ &\times E_\alpha^\dagger (a_2 \dots a_y a_{y+1})_\beta V^\dagger |0_c\rangle, \\ L^{1c}[(1 \dots x)_\alpha, (2 \dots y, y+1)_\beta] \\ &= (-1)^y \sum_{1_c} z(1_c, y+1) \mathcal{A}_{1_c} L[(1 \dots x)_\alpha, (1_c, 2, \dots y)_\beta]. \end{aligned}$$

The operator \mathcal{A}_{1_c} anti-symmetrizes L over the first core index and is defined similarly to \mathcal{A}_{1_e} .

2.1.4. *Single contraction with the valence creation operator:*

1v. Contraction $a_j a_v^\dagger = \delta_{jv}$. The phase $(-1)^{x+y}$ arises due to bringing a_j to the end of $E_\alpha^\dagger C_\beta$ and the phase $(-1)^x$ due to transferring a_i^\dagger to the end of E_α^\dagger . The result reads

$$\{Z|\Phi\}_{1v} = \sum_{\{\alpha\},\{\beta\}} L^{1v}[(1\dots x, x+1)_\alpha, (1\dots y)_\beta] \times (a_1^\dagger \dots a_{x+1}^\dagger)_\alpha C_\beta |0_c\rangle,$$

with

$$L^{1v}[(1\dots x, x+1)_\alpha, (1, 2\dots y)_\beta] = (-1)^y z(x+1, v) L[(1, \dots x)_\alpha, (1, \dots y)_\beta].$$

2.1.5. *Double contractions: one excited and one core operators (1e, 1c).* Here, the number of operators in both core and excited orbitals strings is reduced by 1. The derivation is similar to the 1e case:

$$\{Z|\Phi\}_{1e,1c} = \sum_{\{\alpha\},\{\beta\}} L^{1e,1c}[(2, \dots x)_\alpha, (2, \dots y)_\beta] \times (a_2^\dagger \dots a_x^\dagger)_\alpha (a_2 \dots a_y)_\beta V^\dagger |0_c\rangle, \\ L^{1e,1c}[(2, \dots x)_\alpha, (2, \dots y)_\beta] = (-1)^{x-1} \sum_{1_c, 1_e} z(1_c, 1_e) \mathcal{A}_{1_c} \mathcal{A}_{1_e} \times L[(1_e \dots x)_\alpha, (1_c, \dots y)_\beta].$$

2.1.6. *Double contractions: valence and one core operators (1v, 1c).*

$$\{Z|\Phi\}_{1v,1c} = \sum_{\{\alpha\},\{\beta\}} L^{1v,1c}[(1, \dots x)_\alpha, (2, \dots y)_\beta] \times E_\alpha^\dagger (a_2 \dots a_y)_\beta |0_c\rangle, \\ L^{1v,1c}[(1, \dots x)_\alpha, (2, \dots y)_\beta] = (-1)^y \sum_{1_c} z(1_c, v) \mathcal{A}_{1_c} L[(1, \dots x)_\alpha, (1_c, 2, \dots y)_\beta].$$

2.2. *Example: zeroth-order Hamiltonian*

To illustrate the derived simplification rules, consider a zeroth-order Hamiltonian in the second quantization,

$$H_0 = \sum_i \varepsilon_i : a_i^\dagger a_i : .$$

This is a special case of a one-body operator, equation (11), with $z(i, j) \equiv \varepsilon_i \delta_{ij}$. While the result of applying H_0 to Φ is trivial, arriving at it via the application of the derived rules is instructive. We would like to show that

$$H_0 |\Phi\rangle = (\Sigma_\alpha \varepsilon_\alpha - \Sigma_\beta \varepsilon_\beta + \delta_v \varepsilon_v) |\Phi\rangle. \quad (14)$$

Here $\delta_v = 0$, if there no valence operator present in $|\Phi\rangle$ and $\delta_v = 1$ otherwise. Σ_α is a sum over all indices in the E_α^\dagger string and Σ_β is a sum over core indices in the C_β group.

Because the matrix element $z(i, j) = \varepsilon_i \delta_{ij}$ is diagonal, the only contraction classes which contribute are 1e, 1c and

1v. For example, consider the case of 1e. We deal with the object

$$L^{1e}[(2\dots x, x+1)_\alpha, (1, 2\dots y)_\beta] = (-1)^{x-1} \sum_{1_e} \varepsilon_{x+1} \delta_{1_e, x+1} \mathcal{A}_{1_e} L[(1_e, 2\dots x)_\alpha, (1, \dots y)_\beta] = (-1)^{x-1} \varepsilon_{x+1} \mathcal{A}_{x+1} L[(x+1, 2\dots x)_\alpha, (1, \dots y)_\beta].$$

Then,

$$\{H_0|\Phi\}_{1e} = (-1)^{x-1} \sum_{\{\alpha\}} \sum_{\{\beta\}} \varepsilon_{x+1} \mathcal{A}_{x+1} L[(x+1, 2\dots x)_\alpha, (1, \dots y)_\beta] (a_2^\dagger \dots a_x^\dagger a_{x+1}^\dagger)_\alpha C_\beta V^\dagger |0_c\rangle.$$

Further rename $x+1 \rightarrow 1$ and place the a_1^\dagger at the beginning of the string:

$$\{H_0|\Phi\}_{1e} = \sum_{\{\alpha\}} \sum_{\{\beta\}} \varepsilon_{1_e} \mathcal{A}_{1_e} L[(1_e, 2\dots x)_\alpha, (1, \dots y)_\beta] (a_{1_e}^\dagger \dots a_x^\dagger)_\alpha C_\beta V^\dagger |0_c\rangle.$$

On expanding the partial anti-symmetrization, we encounter terms

$$\sum_{\{\alpha\}} \sum_{\{\beta\}} -\varepsilon_{1_e} L[(\mu, 2, \dots 1_e, \dots x)_\alpha, (1, \dots y)_\beta] \times (a_{1_e}^\dagger \dots a_x^\dagger)_\alpha C_\beta V^\dagger |0_c\rangle.$$

Rename $1_e \leftrightarrow \mu$ and swap the operators

$$\sum_{\{\alpha\}} \sum_{\{\beta\}} +\varepsilon_\mu L[(1_e, 2, \dots \mu, \dots x)_\alpha, (1, \dots y)_\beta] \times (a_{1_e}^\dagger \dots a_x^\dagger)_\alpha C_\beta V^\dagger |0_c\rangle.$$

Therefore,

$$\{H_0|\Phi\}_{1e} = \sum_{\{\alpha\},\{\beta\}} (\Sigma_\alpha \varepsilon_\alpha) L[(1, 2\dots x)_\alpha, (1, 2\dots y)_\beta] E_\alpha^\dagger C_\beta V^\dagger |0_c\rangle.$$

Here, Σ_α is a sum over symbols. Similarly,

$$\{H_0|\Phi\}_{1c} = - \sum_{\{\alpha\},\{\beta\}} (\Sigma_\beta \varepsilon_\beta) L[(1, 2\dots x)_\alpha, (1, 2\dots y)_\beta] \times E_\alpha^\dagger C_\beta V^\dagger |0_c\rangle,$$

and $\{H_0|\Phi\}_{1v} = \varepsilon_v |\Phi\rangle$. All the remaining contractions vanish because they involve matrix elements between core and excited states. Finally, by adding the derived terms we arrive at the well-known formula (14).

2.3. *Contractions with a two-body operator*

Now, we consider products of the two-body part of a two-particle operator G with our generic piece of the many-body wave function, equation (8). We will use

$$G_2 = \frac{1}{4} \sum_{ijkl} \tilde{g}(i, j, k, l) : a_i^\dagger a_j^\dagger a_l a_k : .$$

The derivation is similar to the one-body case of the preceding section. Here, however, the maximum number of possible contractions is 4 and there are 15 distinct cases, enumerated below.

2.3.1. No contractions.

$$\begin{aligned} \{G_2|\Phi\}_0 &= \sum_{\{\alpha\},\{\beta\}} L^0[(1, \dots, x+2)_\alpha, (1, \dots, y+2)_\beta] \\ &\quad \times (E^\dagger a_{x+1}^\dagger a_{x+2}^\dagger)_\alpha (C a_{y+1} a_{y+2})_\beta V^\dagger |0_c\rangle, \\ L^0[(1, \dots, x+2), (1, \dots, y+2)] &= \frac{1}{2} g(x+1, x+2, y+2, y+1) L[(1, \dots, x), (1, \dots, y)]. \end{aligned}$$

2.3.2. Single 1e.

$$\begin{aligned} \{G_2|\Phi\}_{1e} &= \sum_{\{\alpha\},\{\beta\}} L^{1e}[(2, \dots, x+2)_\alpha, (1, \dots, y+1)_\beta] \\ &\quad \times (a_2^\dagger \dots a_{x+1}^\dagger a_{x+2}^\dagger)_\alpha (C a_{y+1})_\beta V^\dagger |0_c\rangle, \\ L^{1e}[(2, \dots, x+2), (1, \dots, y+1)] &= (-1)^{x+y-1} \frac{1}{2} \sum_{1_e} \tilde{g} \\ &\quad \times (x+1, x+2, 1_e, y+1) \mathcal{A}_{1_e} L[(1_e, \dots, x), (1, \dots, y)]. \end{aligned}$$

The partial anti-symmetrization operator \mathcal{A}_{1_e} is given by equation (13).

2.3.3. Single 1c.

$$\begin{aligned} \{G_2|\Phi\}_{1c} &= \sum_{\{\alpha\},\{\beta\}} L^{1c}[(1, \dots, x+2)_\alpha, (2, \dots, y+2)_\beta] \\ &\quad \times (E^\dagger a_{x+1}^\dagger)_\alpha (a_2 \dots a_{y+1} a_{y+2})_\beta V^\dagger |0_c\rangle, \\ L^{1c}[(1, \dots, x+2)_\alpha, (2, \dots, y+2)_\beta] &= \frac{1}{2} \sum_{1_c} \tilde{g} \\ &\quad \times (x+1, 1_c, y+2, y+1) \mathcal{A}_{1_c} L[(1, \dots, x), (1_c, \dots, y)]. \end{aligned}$$

2.3.4. Single 1v.

$$\begin{aligned} \{G_2|\Phi\}_{1v} &= \sum_{\{\alpha\},\{\beta\}} L^{1v}[(1, \dots, x+2)_\alpha, (1, \dots, y+1)_\beta] \\ &\quad \times (E^\dagger a_{x+1}^\dagger a_{x+2}^\dagger)_\alpha (C a_{y+1})_\beta |0_c\rangle, \\ L^{1v}[(1, \dots, x+2)_\alpha, (1, \dots, y+1)_\beta] &= \frac{1}{2} \tilde{g}(x+1, x+2, v, y+1) L[(1, \dots, x), (1, \dots, y)]. \end{aligned}$$

2.3.5. Double 2e.

$$\begin{aligned} \{G_2|\Phi\}_{2e} &= \sum_{\{\alpha\},\{\beta\}} L^{2e}[\dots] (a_3^\dagger \dots a_{x+1}^\dagger a_{x+2}^\dagger)_\alpha C_\beta V^\dagger |0_c\rangle, \\ L^{2e}[\dots] &= \frac{1}{2} \sum_{1_e, 2_e} \tilde{g}(x+1, x+2, 1_e, 2_e) \mathcal{A}_{1_e, 2_e} L \\ &\quad \times [(1_e, 2_e \dots x), (1, \dots, y)]. \end{aligned}$$

The partial anti-symmetrization operator is defined as

$$\begin{aligned} \mathcal{A}_{1,2} f(1, 2, \dots, x) &= f - \sum_{\eta>2} f(1, 2, \dots, \eta, \dots, x)_{\eta \leftrightarrow 1} \\ &\quad - \sum_{\eta>2} f(1, 2, \dots, \eta, \dots, x)_{\eta \leftrightarrow 2} \\ &\quad + \sum_{\eta>v>2} f(1, 2, \dots, v, \dots, \eta, \dots, x)_{v \leftrightarrow 1, \eta \leftrightarrow 2} \end{aligned}$$

(this anti-symmetrization produces $x(x-1)/2$ terms).

As an example, $\mathcal{A}_{1_e, 2_e} \rho_{mn} = \rho_{mn}$ and $\mathcal{A}_{1_e, 2_e} \rho_{mnr} = \rho_{mnr} - \rho_{rnm}$. Alternatively, this definition may be rewritten as

$$\begin{aligned} \mathcal{A}_{1,2} f(1, 2, \dots, x) &= \mathcal{A}_1 f + \mathcal{A}_2 f - f + 2f(2, 1, \dots, x) \\ &\quad + \sum_{\eta>v \geq 3} f(1, 2, \dots, v, \dots, \eta, \dots, x)_{v \leftrightarrow 1, \eta \leftrightarrow 2}. \end{aligned}$$

2.3.6. Double 2c.

$$\begin{aligned} \{G_2|\Phi\}_{2c} &= \sum_{\{\alpha\},\{\beta\}} L^{2c}[\dots] (E^\dagger)_\alpha (a_3 \dots a_{y+1} a_{y+2})_\beta V^\dagger |0_c\rangle, \\ L^{2c}[\dots] &= \frac{1}{2} \sum_{1_c, 2_c} \tilde{g}(2_c, 1_c, y+2, y+1) \mathcal{A}_{1_c, 2_c} L \\ &\quad \times [(1, \dots, x), (1_c, 2_c \dots y)], \end{aligned}$$

where the partial anti-symmetrization operator $\mathcal{A}_{1_c, 2_c}$ is defined similarly to $\mathcal{A}_{1_e, 2_e}$.

2.3.7. Double 1e, 1c.

$$\begin{aligned} \{G_2|\Phi\}_{1e, 1c} &= \sum_{\{\alpha\},\{\beta\}} L^{1e, 1c}[\dots] \\ &\quad \times (a_2^\dagger \dots a_{x+1}^\dagger)_\alpha (a_2 \dots a_{y+1})_\beta V^\dagger |0_c\rangle, \\ L^{1e, 1c}[\dots] &= (-1)^{x+y+1} \sum_{1_e, 1_c} \tilde{g}(x+1, 1_c, 1_e, y+1) \mathcal{A}_{1_e} \mathcal{A}_{1_c} L \\ &\quad \times [(1_e, \dots, x), (1_c, \dots, y)]. \end{aligned}$$

Here, we deal with two successive applications of the partial anti-symmetrization operators introduced in section 2.1, equation (13).

2.3.8. Double 1c, 1v.

$$\begin{aligned} \{G_2|\Phi\}_{1v, 1c} &= \sum_{\{\alpha\},\{\beta\}} L^{1v, 1c}[\dots] (E^\dagger a_{x+1}^\dagger)_\alpha (a_2 \dots a_{y+1})_\beta |0_c\rangle, \\ L^{1v, 1c}[\dots] &= \sum_{1_c, 1_e} \tilde{g}(x+1, 1_c, v, y+1) \mathcal{A}_{1_c} L \\ &\quad \times [(1, \dots, x), (1_c, \dots, y)]. \end{aligned}$$

2.3.9. Double 1e, 1v.

$$\begin{aligned} \{G_2|\Phi\}_{1e, 1v} &= \sum_{\{\alpha\},\{\beta\}} L^{1e, 1v}[\dots] (a_2^\dagger \dots a_{x+1}^\dagger a_{x+2}^\dagger)_\alpha C_\beta |0_c\rangle, \\ L^{1e, 1v}[\dots] &= (-1)^{x+y} \sum_{1_e} g(x+1, x+2, v, 1_e) \mathcal{A}_{1_e} L \\ &\quad \times [(1_e, \dots, x), (1, \dots, y)]. \end{aligned}$$

2.3.10. Triple 2e, 1c.

$$\begin{aligned} \{G_2|\Phi\}_{2e, 1c} &= \sum_{\{\alpha\},\{\beta\}} L^{2e, 1c}[\dots] (a_3^\dagger \dots a_{x+1}^\dagger)_\alpha (a_2 \dots a_y)_\beta V^\dagger |0_c\rangle, \\ (15) \quad L^{2e, 1c}[\dots] &= \sum_{1_c, 1_e, 2_e} \tilde{g}(x+1, 1_c, 1_e, 2_e) \mathcal{A}_{1_e} \mathcal{A}_{1_e, 2_e} L \\ &\quad \times [(1, \dots, x), (1_c, \dots, y)]. \end{aligned}$$

2.3.11. Triple 1e,2c.

$$\{G_2|\Phi\}_{1e,2c} = \sum_{\{\alpha\},\{\beta\}} L^{1e,2c}[\dots](a_2^\dagger \dots a_x^\dagger)_\alpha (a_3 \dots a_{y+1})_\beta V^\dagger |0_c\rangle,$$

$$L^{1e,2c}[\dots] = (-1)^{x+y+1} \sum_{1_e,1_c,2_c} \tilde{g}(2_c, 1_c, 1_e, y+1) \mathcal{A}_{1_e} \mathcal{A}_{1_c,2_c} L$$

$$\times [(1, \dots x), (1_c, \dots y)].$$

2.3.12. Triple 1v,2c.

$$\{G_2|\Phi\}_{1v,2c} = \sum_{\{\alpha\},\{\beta\}} L^{1v,2c}[\dots](E^\dagger)_\alpha (a_3 \dots a_{y+1})_\beta |0_c\rangle,$$

$$L^{1v,2c}[\dots] = \sum_{1_c,2_c} \tilde{g}(2_c, 1_c, v, y+1) \mathcal{A}_{1_c,2_c} L$$

$$\times [(1, \dots x), (1_c, \dots y)].$$

2.3.13. Triple 1e,1v,1c.

$$\{G_2|\Phi\}_{1v,1c,1e} = \sum_{\{\alpha\},\{\beta\}} L^{1v,1c,1e}[\dots]$$

$$\times (a_2^\dagger \dots a_{x+1}^\dagger)_\alpha (a_2 \dots a_y)_\beta |0_c\rangle,$$

$$L^{1v,1c,1e}[\dots] = (-1)^{x+y+1} \sum_{1_c,1_e} \tilde{g}(x+1, 1_c, 1_e, v) \mathcal{A}_{1_c} \mathcal{A}_{1_e} L$$

$$\times [(1, \dots x), (1_c, \dots y)].$$

2.3.14. Quadruple 2e,2c.

$$\{G_2|\Phi\}_{2e,2c} = \sum_{\{\alpha\},\{\beta\}} L^{2e,2c}[\dots]$$

$$\times (a_3^\dagger \dots a_x^\dagger)_\alpha (a_3 \dots a_y)_\beta V^\dagger |0_c\rangle,$$

$$L^{2e,2c}[\dots] = \sum_{1_e,2_e,1_c,2_c} \tilde{g}(2_c, 1_c, 1_e, 2_e) \mathcal{A}_{1_e,2_e} \mathcal{A}_{1_c,2_c} L$$

$$\times [(1, \dots x), (1_c, \dots y)].$$

2.3.15. Quadruple 1e,1v,2c.

$$\{G_2|\Phi\}_{1v,1e,2c} = \sum_{\{\alpha\},\{\beta\}} L^{1v,1e,2c}[\dots]$$

$$\times (a_2^\dagger \dots a_x^\dagger)_\alpha (a_3 \dots a_y)_\beta |0_c\rangle,$$

$$L^{1v,1e,2c}[\dots] = (-1)^{x+y+1} \sum_{1_e,1_c,2_c} \tilde{g}(2_c, 1_c, 1_e, v) \mathcal{A}_{1_e} \mathcal{A}_{1_c,2_c} L$$

$$\times [(1, \dots x), (1_c, \dots y)].$$

2.4. Additional remarks

Note that the introduced partial anti-symmetrization operators, equations (13), (15), are subsumed into the following general definition of a partial anti-symmetrization operator $\mathcal{A}[\{1, \xi\}_\gamma, \{1, \mu\}_\delta]$ over a subset $\{1, \xi\}$ of excited indices and a subset $\{1, \mu\}$ of core indices

$$\mathcal{A}[\{1, \xi\}_\gamma, \{1, \mu\}_\delta] L[(1, 2 \dots x)_\alpha, (1, 2 \dots y)_\beta]$$

$$= \sum \sum \{F[(1, 2 \dots x)_\alpha] F[(1, 2 \dots y)_\beta] L$$

$$\times [(1, 2 \dots x)_\alpha, (1, 2 \dots y)_\beta]\}_{(\gamma_i \longleftrightarrow \alpha_j, \delta_i \longleftrightarrow \beta_j)}.$$

Here, the summation is over all possible renaming of indices in the groups. Individual phases of the terms are determined by functions F which we use to denote the conventionally defined signature of the resulting permutation of indices.

The derived rules may be presented in a more symmetric form by noticing that no matter how simple or complicated the dependence on the indices inside the object L is, by systematically swapping the dummy summation indices the generic piece of MBPT wavefunction, equation (10), may be rewritten as

$$|\Phi\rangle = \frac{1}{x!y!} \sum_{\{\alpha\},\{\beta\}} \tilde{L}[(1, 2 \dots x)_\alpha, (1, 2 \dots y)_\beta] E_\alpha^\dagger C_\beta V^\dagger |0_c\rangle,$$

where the object \tilde{L} was obtained by a complete anti-symmetrization of L inside of the groups of excited and core indices. In other words, in the derived theorems, one could simply replace

$$L[\dots] \rightarrow \frac{1}{x!y!} \tilde{L}[\dots]$$

and unfold the partial anti-symmetrization operators. While the resulting expressions may be more aesthetically appealing, we did not find any particular advantage in using them in practical calculations.

3. Observables

The application of the derived rules allows us to find many-body correction to atomic wavefunction in an arbitrary order of MBPT via equation (8). Below we focus on an efficient symbolic evaluation of expressions for MBPT correction to energies and matrix elements.

3.1. Corrections to energy

The correlation correction to energy in the n th order of MBPT may be found with the $(n-1)$ th-order correction to the wavefunction

$$\delta E^{(n)} = \langle \Psi^{(0)} | V_I | \Psi^{(n-1)} \rangle, \quad (16)$$

or in the frozen-core approximation for mono-valent atoms,

$$\delta E^{(n)} = \langle 0_c | a_v \{G_2 | \Psi_v^{(n-1)}\} \rangle. \quad (17)$$

Now, we focus on the object in the curly brackets, $|\phi\rangle = G_2 | \Psi_v^{(n-1)} \rangle$. We may use the results of section 2.3 and derive a multitude of the terms on the right-hand side. Ultimately determination of the energy correction is simplified by noticing that only a small number of terms would remain after forming the required product $\langle 0_c | a_v | \phi \rangle$. The non-vanishing contributions arise from generic pieces

$$\{G_2 | \Psi^{(n-1)}\}_v = L_c [(0) | a_v^\dagger | 0_c \rangle,$$

where L_c does not depend on the valence orbital, and

$$\{G_2 | \Psi^{(n-1)}\}_e = \sum_{1_e} L_v [(1_e) | a_{1_e}^\dagger | 0_c \rangle,$$

where L_v necessarily depends on the valence index. Accordingly, the corrections to the energy may be separated into the core and valence parts,

$$\delta E^{(n)} = \delta E_c^{(n)} + \delta E_v^{(n)},$$

with $\delta E_c^{(n)} = L_c$ and $\delta E_v^{(n)} = L_v [(v) | 0_c \rangle$. This solves the problem of finding the energy correction.

3.2. Matrix elements of a one-body operator Z

Suppose we derived the MBPT corrections to wavefunctions of two valence states w and v . We would like to compute the matrix element of some one-particle operator Z . To this end, we need to use the formula (9) and compute terms

$$\langle \Psi_w^{(n-k-1)} | Z_1 | \Psi_v^{(k)} \rangle.$$

We start by introducing an intermediate state

$$|\psi_v\rangle = Z_1 |\Psi_v^{(k)}\rangle.$$

Then, our task will be accomplished by forming the product $\langle \Psi_w^{(n-k-1)} | \psi_v \rangle$.

$|\psi_v\rangle$ may be computed using rules of section 2.1. It will contain a linear combination of various ‘generic contributions’; we focus on a scalar product of generic contributions to $|\psi_v\rangle$

$$|\Phi_v\rangle = \sum_{\{\alpha\}, \{\beta\}} L[(1, 2 \dots x)_\alpha, (1, 2 \dots y)_\beta] E_\alpha^\dagger C_\beta V^\dagger |0_c\rangle$$

and to $\langle \Psi_w^{(n-k-1)} |$

$$\langle \Phi_w | = \sum_{\{\alpha'\}, \{\beta'\}} K[(1, 2 \dots x')_{\alpha'}, (1, 2 \dots y')_{\beta'}] \langle 0_c | W C_{\beta'}^\dagger E_{\alpha'}.$$

We adopt a convention that in the groups of operators $C_{\beta'}^\dagger$ and $E_{\alpha'}$ the enumeration of operator indices goes from right to left, i.e. $C_{\beta'}^\dagger = a_{y'}^\dagger \dots a_2^\dagger a_1^\dagger$ and $E_{\alpha'} = a_{x'} \dots a_2 a_1$.

To obtain a nonzero value for the scalar product $\langle \Phi_w | \Phi_v \rangle$, we have to perform a maximum number of contractions. Moreover, the numbers of operators must be related as $x + \delta_v = x' + \delta_w$ and $y = y'$.

We contract the core orbitals first. Bringing the two groups of operators together introduces a phase factor of $(-1)^{(x-x')}$ and we obtain

$$\begin{aligned} \langle \Phi_w | \Phi_v \rangle &= (-1)^{(x-x')} \sum_{\{\alpha'\}, \{\alpha\}} \sum_{\{\beta\}} \langle 0_c | W E_{\alpha'} E_\alpha^\dagger V^\dagger | 0_c \rangle \\ &L[(1, 2 \dots x)_\alpha, (1, 2 \dots y)_\beta] \mathcal{A}_{\{\beta\}} K \\ &\times [(1, 2 \dots x')_{\alpha'}, (1, 2 \dots y)_\beta]. \end{aligned}$$

Here, $\mathcal{A}_{\{\beta\}}$ denotes a complete anti-symmetrization over all indices in the symbolic set $\{\beta\}$. The result may be proven by noticing that the complete contraction between the products $C_{\beta'}^\dagger C_\beta$ may be expressed as

$$C_{\beta'}^\dagger C_\beta = \det \begin{vmatrix} \delta_{11'} & \delta_{12'} & \dots & \delta_{1x'} \\ \delta_{21'} & \delta_{22'} & \dots & \delta_{2x'} \\ \vdots & \vdots & \ddots & \vdots \\ \delta_{x1'} & \delta_{x2'} & \dots & \delta_{xx'} \end{vmatrix}.$$

The result of computing the remaining product $\langle 0_c | W E_{\alpha'} E_\alpha^\dagger V^\dagger | 0_c \rangle$ depends on whether we have the valence operators present inside the w and V^\dagger groups; we treat three separate cases below.

3.2.1. Both valence operators are absent. In this case, both objects, L and K , necessarily depend on their respective valence indices and we emphasize these dependences by superscripts L^v and k^w . Also $x = x'$ and (similar to full contraction for core orbitals)

$$\begin{aligned} \langle \Psi_w | \Phi_v \rangle_{\text{val}} &= \sum_{\{\alpha\}} \sum_{\{\beta\}} L^v[(1, 2 \dots x)_\alpha, (1, 2 \dots y)_\beta] \mathcal{A}_{\{\alpha\}} \mathcal{A}_{\{\beta\}} K^w \\ &\times [(1, 2 \dots x)_\alpha, (1, 2 \dots y)_\beta]. \end{aligned}$$

Such a combination produces $x!y!$ diagrams.

3.2.2. Only one valence operator is present. Consider first the case when only the operator a_v^\dagger is present, then the object K depends on the index w ; we denote this dependence as k^w . Also $x' = x + 1$. By appending a_v^\dagger at the end of the E_α^\dagger string, we reduce the treatment of contractions to the preceding case:

$$\begin{aligned} \langle \Psi_w | \Phi_v \rangle &= (-1)^y \sum_{\{\alpha'\}, \{\alpha\}} \sum_{\{\beta\}} \langle 0_c | E_{\alpha'} E_\alpha^\dagger a_v^\dagger | 0_c \rangle L \\ &\times [(1, 2 \dots x)_\alpha, (1 \dots y)_\beta] \mathcal{A}_{\{\beta\}} K^w \\ &\times [(1', 2' \dots x')_{\alpha'}, (1 \dots y)_\beta], \end{aligned}$$

$$\begin{aligned} \langle \Psi_w | \Phi_v \rangle_v &= (-1)^y \sum_{\{\alpha\}} \sum_{\{\beta\}} L[(1, 2 \dots x)_\alpha, \\ &(1 \dots y)_\beta] \mathcal{A}_{\{\alpha\}} \mathcal{A}_{\{\beta\}} K^w [(1, 2 \dots x, v)_\alpha, (1 \dots y)_\beta]. \end{aligned}$$

If only a_w is present, then

$$\begin{aligned} \langle \Psi_w | \Phi_v \rangle_w &= (-1)^y \sum_{\{\alpha'\}} \sum_{\{\beta\}} K[(1', 2' \dots x')_{\alpha'}, \\ &(1 \dots y)_\beta] \mathcal{A}_{\{\alpha\}} \mathcal{A}_{\{\beta\}} L^v [(1', 2' \dots x', w)_\alpha, (1 \dots y)_\beta]. \end{aligned}$$

3.2.3. Both valence operators are present. If both valence operators are present, i.e. $W = a_w$ and $V^\dagger = a_v^\dagger$, then $x = x'$. The product $\langle 0_c | a_w E_{\alpha'} E_\alpha^\dagger a_v^\dagger | 0_c \rangle$ may be broken into two contributions.

(i) Contraction between a_w and a_v^\dagger leads to a core contribution

$$\begin{aligned} \langle \Psi_w | \Phi_v \rangle_c^{x=x'} &= \delta_{wv} \sum_{\{\alpha\}} \sum_{\{\beta\}} L[(1, \dots x)_\alpha, \\ &(1, \dots y)_\beta] \mathcal{A}_{\{\alpha\}} \mathcal{A}_{\{\beta\}} K[(1, \dots x)_\alpha, (1, \dots y)_\beta]. \end{aligned} \quad (18)$$

Note that this contribution vanishes for $w \neq v$ and, moreover, it does not vanish only in a very special case of true scalar operator Z .

(ii) Simultaneous contractions between a_w and an operator in E_α^\dagger , a_v^\dagger with an operator in $E_{\alpha'}$ and residual contractions lead to $(y!x!)x$ contributions

$$\begin{aligned} \langle \Psi_w | \Phi_v \rangle_{\text{val}} &= - \sum_{\{\alpha\}} \sum_{\{\beta\}} \sum_{\xi \in \{\alpha\}} S L[(1, \dots x)_\alpha, \\ &(1, \dots y)_\beta]_{\xi \rightarrow w} \mathcal{A}_{\{\alpha\}} \mathcal{A}_{\{\beta\}} K[(1, 2 \dots x)_\alpha, (1, \dots y)_\beta]_{\xi \rightarrow v} \end{aligned}$$

Here, $S_{\xi \in \{\alpha\}}$ represents a summation over all possible simultaneous replacement of index ξ by w in L and by v in K .

Table 1. Complexity of MBPT for mono-valent systems in the frozen-core approximation. We list numbers of diagrams in the n th order of MBPT for wavefunctions and matrix elements of a one-particle operator. There are two counts for $Z_{wv}^{(n)}$ in the format n_1/n_2 . n_1 is a number of terms in a maximally simplified expression (where the Coulomb integrals g_{ijkl} were combined into the anti-symmetric combinations \tilde{g}_{ijkl}). n_2 is the full number of the conventional Brueckner–Goldstone diagrams including exchange diagrams.

Order n	$ \Psi_v^{(n)}\rangle$	$Z_{wv}^{(n)}$
0	1	–
1	2	1/1
2	20	2/4
3	561	30/84
4	26 700	552/3072

4. Counting diagrams and summary

The present paper provides symbolic prescriptions to aid in deriving many-body diagrams for mono-valent systems in an arbitrary order of MBPT. Based on the derived rules, the author has developed a Mathematica package, which is made available through the author’s website [17]. The rules have been tested by recovering known results for matrix elements and energies through the third order [10]. Note that the package and the theorems have been already used in deriving matrix elements through the fourth order of MBPT [15, 16].

The derived rules are certainly not as mnemonically elegant as the original Wick’s theorem; this is a reflection of the fact that the Wick theorem is formulated in terms of the pairwise contractions between the operators, while our rules provide an explicit (yet general) answer that avoids a multitude of elemental pairwise contractions. In this sense, the derived theorems may be called ‘post-Wick’ theorems.

As an illustration, we derive the MBPT diagrams for matrix elements of a one-body operator between two distinct states w and v of a mono-valent atom. We run the package and obtain analytical expressions for the diagrams. The expressions are too lengthy to be presented here (see, however, a partial list of fourth-order diagrams in [15]); instead we count the number of resulting diagrams. The results are compiled in table 1. The counts do not include the normalization term of equation (9) and the core contribution (18).

As discussed, due to our short-cutting the expensive elemental pairwise contractions, the advantage of the present formulation becomes most pronounced in high orders of perturbation theory, as both the number of resulting terms

rapidly grows (see table 1) and the length of operator strings entering $|\Psi^{(n)}\rangle$ increases with n . In addition, from a practical standpoint, in symbolic algebra implementations, the next step involves combining similar terms by pattern matching. This is a computationally expensive search operation. By contrast to the directly applied Wick’s expansion method, our derived theorems already yield simplified results, further speeding up the symbolic evaluations.

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