# Contents

# 1 Cumulants, extensivity, and the connected formulation of the contracted Schrödinger equation

JOHN M. HERBERT[†] and JOHN E. HARRIMAN[‡]

Department of Chemistry, The Ohio State University, Columbus, OH 43210
Department of Chemistry, University of Wisconsin, Madison, WI 53706

## 1.1 INTRODUCTION

In recent years, several groups [1–16] have explored the possibility of circumventing the wave function and the electronic Schrödinger equation in quantum chemical calculations, instead solving the so-called contracted Schrödinger equation (CSE)[16–19] for the two-electron reduced density matrix (2-RDM). Within the set of $N$-representable[20–24] RDMs, the CSE is an equivalent [16,18] formulation of the $N$-electron, clamped-nuclei Schrödinger equation, and couples the 2-, 3-, and 4-RDM elements via a linear equation that does not involve the electronic wave function explicitly. Direct calculation of the 2-RDM, and thereby electronic properties, is accomplished using approximate *reconstruction functionals*, [7–9,15,25–27] by means of which the 3- and 4-RDMs are expressed in terms of the 2-RDM, leading to closed nonlinear equations for matrix elements of the latter.

Much of the recent literature on RDM reconstruction functionals is couched in terms of cumulant decompositions. [13,27–38] Insofar as the $p$-RDM represents a quantum-mechanical probability distribution for $p$-electron subsystems of an $N$-electron super-system, the RDM cumulant formalism bears much similarity to the cumulant formalism of classical statistical mechanics, as formalized long ago by by Kubo. [39] (Quantum mechanics introduces important differences, however, as we shall discuss.) Within the cumulant formalism, the $p$-RDM is decomposed into “con-

---

[†] Ohio State University (`jherbert@chemistry.ohio-state.edu`)
[‡] University of Wisconsin

nected" and "unconnected" contributions, with the latter obtained in a known way from the lower-order $q$-RDMs, $q < p$. The connected part defines the $p$th-order RDM cumulant ($p$-RDMC). In contrast to the $p$-RDM, the $p$-RDMC is an *extensive* quantity, meaning that it is additively separable in the case of a composite system composed of non-interacting subsystems. (The $p$-RDM is multiplicatively separable in such cases.[28,32]) The implication is that the RDMCs, and the connected equations that they satisfy, behave correctly in the limit of non-interacting subsystems *by construction*, whereas a 2-RDM obtained by approximate solution of the CSE may fail to preserve extensivity, or in other words may not be *size-consistent*.[40–42]

In this work, we derive—via explicit cancellation of unconnected terms in the CSE—a pair of simultaneous, connected equations that together determine the 1- and 2-RDMCs, which in turn determine the 2-RDM in a simple way. Because the cancellation of unconnected terms is exact, we have in a sense done nothing; the connected equations are equivalent to the CSE and, given $N$-representability boundary conditions, they are also equivalent to the electronic Schrödinger equation. The important difference is that the connected equations for the cumulants automatically yield a size-consistent 2-RDM, even when solved approximately, because every term in these equations is manifestly extensive.

The derivation of the connected equations that is presented here is an expanded version of the one we published previously.[43] Our derivation utilizes a diagram technique and a "first-quantized" formalism, in which the CSE is expressed in terms of position-space kernels and Hilbert-space operators. Equations that couple the RDMCs have also been published in second quantization, by Kutzelnigg and Mukherjee[29–31] and by Nooijen *et al.*,[44] but the derivation presented here has the conceptual advantage that it explicitly demonstrates the cancellation of all unconnected terms, and furthermore does not require the introduction of a basis set (as is tacitly assumed in second quantization). Our derivation thus proves that the final, connected equations are equivalent to the CSE as well as to the ordinary electronic Schrödinger equation. Moreover, our derivation clarifies several important differences between the connected and the unconnected equations. As explained in Section 1.5.2, the connected CSE is in fact a pair of *implicit* equations for the 1- and 2-RDMCs, whereas the original CSE is an *explicit* equation for the RDMs. In addition, the electronic energy—an explicit parameter in the CSE—is absent from this equation's connected analogues. Formally speaking, the connected equations that we ultimately obtain are equivalent to the "irreducible" CSEs introduced by Kutzelnigg and Mukherjee,[29–31] who derived connected equations starting from the fermion anticommutation relations, in a manner that does not rely upon the original CSE at all.

The remainder of this chapter is organized as follows. Section 1.2 introduces the CSE as a special case of a more general class of *reduced eigenvalue equations*, and Section 1.3 formally defines the RDMCs. In the interest of motivating our derivation of connected CSEs, we include in Section 1.3 a survey of the quantum-mechanical cumulant formalism and the basic properties of the RDMCs, focusing especially on their additive separability for non-interacting subsystems. In Section 1.4, we develop a diagram technique to facilitate formal manipulation of terms that appear in the CSE. These diagrams also clarify the relationship between the CSE and older, Green's function methods in many-body theory, a connection that is examined in Section 1.5. In that section we also present the main result of this work, a derivation of the connected form of the CSE, along with a discussion of procedures for solving the connected equations.

## 1.2 REDUCED EIGENVALUE EQUATIONS

Employing the abbreviated notation "$j$" $\equiv \mathbf{x}_j$ for the composite space/spin coordinates of the $j$th electron, let

$$\hat{W}(1,\ldots,N) = \sum_{j=1}^{N} \hat{h}(j) + \sum_{j<k}^{N} \hat{g}(j,k) \tag{1.1}$$

be a symmetric operator on the $N$-electron Hilbert space. This implies that $\hat{g}(j,k) = \hat{g}(k,j)$, which reflects the indistinguishability of electrons. We wish to consider RDM analogues of the $N$-electron eigenvalue equation

$$\hat{W}\Psi = w\Psi\ . \tag{1.2}$$

Let the eigenvalue $w$ be fixed and assume that $\Psi$ is nondegenerate and unit-normalized. The restriction to nondegenerate eigenstates will be relaxed in Section 1.5, but for now we consider only pure-state density matrices. The $N$-electron density matrix for the pure state $\Psi$ is

$$D_N(1,\ldots,N;1',\ldots,N') \overset{\text{def}}{=} \Psi(1,\ldots,N)\ \Psi^*(1',\ldots,N')\ . \tag{1.3}$$

For $p < q \leq N$, we define a *partial trace operator*

$$\text{tr}_{p+1,\ldots,q} \overset{\text{def}}{=} \int d\mathbf{x}_{p+1}\cdots d\mathbf{x}_q\ d\mathbf{x}'_{p+1}\cdots d\mathbf{x}'_q\ \delta(\mathbf{x}_{p+1}-\mathbf{x}'_{p+1})\cdots\delta(\mathbf{x}_q-\mathbf{x}'_q) \tag{1.4}$$

that generates the $p$-RDM from the $q$-RDM,

$$D_p = \left[\frac{q!(N-q)!}{p!(N-p)!}\right] \text{tr}_{p+1,\ldots,q}\, D_q\ , \tag{1.5}$$

and furthermore establishes the normalization

$$\text{tr}\, D_p \equiv \text{tr}_{1,\ldots,p}\, D_p = \binom{N}{p}\ . \tag{1.6}$$

This is the convention that is most convenient for calculating expectation values, since in this case $\langle\Psi|\hat{W}|\Psi\rangle = \text{tr}\,(\hat{W}_2\,D_2)$, where

$$\hat{W}_{2(1,2)} \overset{\text{def}}{=} \hat{g}(1,2) + \frac{\hat{h}(1) + \hat{h}(2)}{N-1} \tag{1.7}$$

is the two-electron *reduced operator* corresponding to $\hat{W}$.[45,46]

Most of this chapter utilizes the first-quantized formulation of the RDMs introduced above. However, some concepts related to separability and extensivity are more easily discussion in second quantization, and the second-quantized formalism is therefore employed in Section 1.3. Introducing an orthonormal spin orbital basis $|\phi_j\rangle = \hat{a}_j^\dagger|0\rangle$, the elements of the $p$-RDM are expressed directly in second quantization as

$$\mathbf{D}_{i_1,\ldots,i_p;j_1,\ldots,j_p} = \frac{1}{p!}\langle\Psi|\,\hat{a}_{i_1}^\dagger \cdots \hat{a}_{i_p}^\dagger\,\hat{a}_{j_p} \cdots \hat{a}_{j_1}\,|\Psi\rangle\;. \tag{1.8}$$

We denote the tensor of such elements as $\mathbf{D}_{\boldsymbol{p}}$, which is the tensor representation of the kernel $D_p$ in a basis of $p$-electron direct products of the spin orbitals $\{|\phi_j\rangle\}$.[46] The convention introduced in Eq. (1.8), that the number of indices implicitly specifies the tensor rank, is followed wherever tensors are used in this chapter.

From the $N$-electron Hilbert-space eigenvalue equation, Eq. (1.2), follows a hierarchy of $p$-electron *reduced* eigenvalue equations,[13,17,18,47] for $1 \le p \le N-2$. The $p$th equation of this hierarchy couples $D_p$, $D_{p+1}$, and $D_{p+2}$, and can be expressed as

$$\Omega_{p(1,\ldots,p;1',\ldots,p')} \equiv 0\,, \tag{1.9}$$

in which $\Omega_p$ is the $p$-electron kernel[11]

$$\begin{aligned}\Omega_{p(1,\ldots,p;1',\ldots,p')} \overset{\text{def}}{=} &\left[\sum_{j=1}^{p}\hat{h}(j) + (1-\delta_{p,1})\sum_{j<k}^{p}\hat{g}(j,k) - w\right]D_p \\ &+ (p+1)\text{tr}_{p+1}\left\{\left[\hat{h}(p+1) + \sum_{j=1}^{p}\hat{g}(j,p+1)\right]D_{p+1}\right\} \\ &+ \binom{p+2}{2}\text{tr}_{p+1,p+2}\left\{\hat{g}(p+1,p+2)\,D_{p+2}\right\}\,.\end{aligned} \tag{1.10}$$

Here $D_n = D_{n(1,\ldots,n;1',\ldots,n')}$. The quantity $\Omega_p$ is called the $p$th-order *energy density matrix*.

Following Kutzelnigg and Mukherjee,[29–31] we refer to Eq. (1.9) the $p$th-order CSE, or CSE($p$) for brevity. [CSE($p$) has also been called the $(p, p+2)$-CSE.[13]] Strictly speaking, the term "CSE" implies that $\hat{W}$ is an electronic Hamiltonian, which is clearly the most important case, but the formal structure of Eqs. (1.9) and (1.10) is the same for any $\hat{W}$ having the form specified in Eq. (1.1). In the case of spin eigenstates, for example, the reduced equations for $\hat{W} = \hat{S}^2$ may be useful as boundary conditions to enforce while solving CSE($p$).[3]

The remarkable fact, first demonstrated by Nakatsuji,[18] is that for each $p \geq 2$, CSE($p$) is equivalent (in a necessary and sufficient sense) to the original Hilbert-space eigenvalue equation, Eq. (1.2), provided that CSE($p$) is solved subject to boundary conditions ($N$-representability conditions) appropriate for the $(p+2)$-RDM. CSE($p$), in other words, is a closed equation for the $(p+2)$-RDM [which determines the $(p+1)$- and $p$-RDMs by partial trace], and has a unique $N$-representable solution $D_{p+2}$ for each electronic state, including excited states. Absent $N$-representability constraints, however, this equation has many spurious solutions.[48,49] CSE(2) is the most tractable reduced equation that is still equivalent to the original Hilbert-space equation, and ultimately it is CSE(2) that we wish to solve. Importantly, we do not wish to solve CSE(2) for the 4-RDM, as this quantity is an eight-index tensor subject to four-electron $N$-representability conditions. Rather, we wish to solve CSE(2) in terms of the 2-RDM, via reconstruction of the 3- and 4-RDMs.

## 1.3 REDUCED DENSITY MATRIX CUMULANTS

In this section we introduce the $p$-RDMC, $\Delta_p$, which encapsulates the part of the $p$-RDM that is additively separable in the limit of non-interacting subsystems. Although the RDMCs have been discussed at length in the literature,[27–38] this section provides an introduction and summary of the most important points. In this section we use the second-quantized formulation of the RDMs [see Eq. (1.8)], as separability properties are most easily introduced using this formalism.

### 1.3.1 Additive versus multiplicative separability

Although the RDMs provide a compact and appealing description of electronic structure, this description is unsatisfactory in at least one respect, namely, expectation values calculated from RDMs are not *manifestly* extensive, so do not necessarily become additively separable in the limit of non-interacting subsystems. This basic flaw ultimately arises because the RDMs are multiplicatively separable rather than additively separable.[28,32]

To illustrate this point, consider a composite system composed of two non-interacting subsystems, one with $p$ electrons (subsystem A) and the other with $q = N - p$ electrons (subsystem B). This would be the case, for example, in the limit that a diatomic molecule A–B is stretched to infinite bond distance. Because subsystems A and B are non-interacting, there must exist disjoint sets $\mathcal{B}_\mathrm{A}$ and $\mathcal{B}_\mathrm{B}$ of orthonormal spin orbitals, one set associated with each subsystem, such that the composite system's Hamiltonian matrix can be written as a direct sum

$$\mathbf{H} = \mathbf{H}_\mathrm{A} \oplus \mathbf{H}_\mathrm{B} \ , \tag{1.11}$$

where $\mathbf{H}_{\mathrm{X}}$ ($\mathrm{X} \in \{\mathrm{A}, \mathrm{B}\}$) consists of matrix elements between determinants $\Phi_{\mathrm{X}}$ constructed exclusively from spin orbitals in $\mathcal{B}_{\mathrm{X}}$. Thus $\langle \Phi_{\mathrm{A}} | \hat{H} | \Phi_{\mathrm{B}} \rangle = 0$.

Let $\Psi_{\mathrm{X}}$ be an eigenfunction of $\mathbf{H}_{\mathrm{X}}$, normalized to unity. Then the wave function for the composite system is

$$\Psi(1,\ldots,N) = \frac{1}{\sqrt{N!}} \, \hat{\mathsf{P}}_N \big( \Psi_{\mathrm{A}}(1,\ldots,p) \; \Psi_{\mathrm{B}}(p+1,\ldots,N) \big) \;, \tag{1.12}$$

in which the operator $\hat{\mathsf{P}}_N$ antisymmetrizes the product function $\Psi_{\mathrm{A}} \Psi_{\mathrm{B}}$ by generating all $N!$ signed permutations of the coordinates $\mathbf{x}_1, \ldots, \mathbf{x}_N$. In Dirac notation, $|\Psi\rangle = |\Psi_{\mathrm{A}} \Psi_{\mathrm{B}}\rangle$, and one says that $\Psi$ is *multiplicatively separable* in the two subsystems, recognizing that in quantum mechanics $|\Psi\rangle$ is separable only up to an overall antisymmetrization (or a symmetrization, in the case of bosons) that renders all coordinates equivalent. The separation of the wave function in Eq. (1.12) is equivalent, in a necessary and sufficient sense, to the block structure of the Hamiltonian in Eq. (1.11).[32,50–52]

Because subsystems A and B do not interact, it must be that $\Psi_{\mathrm{A}}$ consists of a determinantal expansion in functions $\Phi_{\mathrm{A}}$ taken solely from the set $\mathcal{B}_{\mathrm{A}}$, and similarly $\Psi_{\mathrm{B}}$ uses only those spin orbitals in $\mathcal{B}_{\mathrm{B}}$. It follows that $\Psi_{\mathrm{A}}$ and $\Psi_{\mathrm{B}}$ are strongly orthogonal.[53] Two antisymmetric functions $f(x_1, \ldots, x_p)$ and $g(y_1, \ldots, y_q)$ are said to be *strongly orthogonal* if

$$\int dz \; f^*(x_1, \ldots, x_{p-1}, z) \; g(y_1, \ldots, y_{q-1}, z) \equiv 0 \;. \tag{1.13}$$

Note that the integral above is nominally a function of $p+q-2$ coordinates. Furthermore, because the functions of interest are antisymmetric, it does not matter which coordinates are chosen for the dummy integration variable $z$.

Consider the RDMs obtained from the separable wave function in Eq. (1.12). Since $\Psi_{\mathrm{A}}$ and $\Psi_{\mathrm{B}}$ are strongly orthogonal, it follows from Eq. (1.8) that $\langle \Psi_{\mathrm{A}} \Psi_{\mathrm{B}} | \hat{a}_i^\dagger \, \hat{a}_j | \Psi_{\mathrm{A}} \Psi_{\mathrm{B}} \rangle = 0$ unless $\phi_i$ and $\phi_j$ are associated with the same subsystem. Thus the 1-RDM separates into subsystem 1-RDMs,

$$D_1(\mathbf{x}; \mathbf{x}') = D_1^{\mathrm{A}}(\mathbf{x}; \mathbf{x}') + D_1^{\mathrm{B}}(\mathbf{x}; \mathbf{x}') \;. \tag{1.14}$$

The case $p = 1$ is the unique example for which $D_p$ is additively separable. This is equivalent to the statement that $D_1$ equals its own cumulant (see Section 1.3.2).

To obtain $D_2$, we need to evaluate matrix elements $\langle \Psi_{\mathrm{A}} \Psi_{\mathrm{B}} | \hat{a}_i^\dagger \, \hat{a}_j^\dagger \, \hat{a}_l \, \hat{a}_k | \Psi_{\mathrm{A}} \Psi_{\mathrm{B}} \rangle$. For reasons that will become clear, let us introduce the quantity

$$\boldsymbol{\Delta}_{ij;kl} \overset{\text{def}}{=} \mathbf{D}_{ij;kl} - \tfrac{1}{2} \big( \mathbf{D}_{i;k} \, \mathbf{D}_{j;l} - \mathbf{D}_{i;l} \, \mathbf{D}_{j;k} \big) \;. \tag{1.15}$$

The interesting scenario is when two of the four indices in this equation refer to subsystem A and the other two refer to subsystem B. Suppose, for definiteness, that $\phi_i, \phi_j \in \mathcal{B}_{\mathrm{A}}$ and $\phi_k, \phi_l \in \mathcal{B}_{\mathrm{B}}$. Then the strong orthogonality of $\Psi_{\mathrm{A}}$ and $\Psi_{\mathrm{B}}$ implies that $\mathbf{D}_{ij;kl} = 0$. More interesting is the case when $\phi_i, \phi_k \in \mathcal{B}_{\rm A}$ and $\phi_j, \phi_l \in \mathcal{B}_{\rm B}$. In this case $\mathbf{D}_{ij;kl}$ is generally nonzero, hence $D_2$ mixes indices from different non-interacting subsystems, and thus fails to be additively separable. What about $\boldsymbol{\Delta}_{ij;kl}$? According to Eq. (1.14), $\mathbf{D}_{i;l} = 0$ since $i$ and $l$ refer to different subsystems, and therefore $\boldsymbol{\Delta}_{ij;kl} = \mathbf{D}_{ij;kl} - \frac{1}{2}\,\mathbf{D}_{i;k}\,\mathbf{D}_{j;l}$. The 2-RDM part of this expression can be simplified using the anticommutation relations, noting that $i \neq l$ and $j \neq k$. The result is

$$\begin{aligned} \mathbf{D}_{ij;kl} &\equiv \tfrac{1}{2}\langle \Psi_{\rm A}\Psi_{\rm B}|\hat{a}_i^\dagger\,\hat{a}_k\,\hat{a}_j^\dagger\,\hat{a}_l|\Psi_{\rm A}\Psi_{\rm B}\rangle \\ &= \tfrac{1}{2}\langle \Psi_{\rm A}|\hat{a}_i^\dagger\,\hat{a}_k|\Psi_{\rm A}\rangle\,\langle \Psi_{\rm B}|\hat{a}_j^\dagger\,\hat{a}_l|\Psi_{\rm B}\rangle \;, \end{aligned} \tag{1.16}$$

which is a product of 1-RDM elements from different subsystems. It follows that $\boldsymbol{\Delta}_{ij;kl} = 0$ for the case in question, and since $\boldsymbol{\Delta}_{ij;kl}$ as defined in Eq. (1.15) is antisymmetric, this quantity must in fact be zero unless all four indices refer to the same subsystem. Thus, unlike $\mathbf{D}_{ij;kl}$, the quantity $\boldsymbol{\Delta}_{ij;kl}$ is additively separable in the two non-interacting subsystems A and B,

$$\Delta_2(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') = \Delta_2^{\rm A}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') + \Delta_2^{\rm B}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2') \;. \tag{1.17}$$

$\Delta_2$ is precisely the 2-RDMC, and from Eq. (1.15) we note that expectation values for the composite $\rm A + B$ system can be computed using either $D_2$ alone, or $D_1 \equiv \Delta_1$ together with $\Delta_2$. From the standpoint of *exact* quantum mechanics, either method yields exactly the same expectation value and, in particular, both methods respect the extensivity of the electronic energy. If $D_2$ is calculated by means of *approximate* quantum mechanics, however, one cannot generally expect that extensivity will be preserved, since exchange terms mingle the coordinates on different subsystems, and exact cancellation cannot be anticipated unless built in from the start. Methods that respect this separability by construction are said to be size-consistent.[40–42]

In careful usage, extensivity is actually a more general concept than size consistency.[42] The former term implies a complete absence of unconnected terms in one's working equations, while size-consistency merely indicates that the energy is additively separable for non-interacting subsystems, a necessary consequence of extensivity. Methods that violate extensivity will yield per-particle correlation energies that tend to zero in the limit of an infinite system.[42] Hence the conventional wisdom is that use of manifestly extensive methods (coupled-cluster theory being the canonical example) is crucial for "large" systems containing sub-units so distant as to be essentially non-interacting. It is not entirely clear how large one can go before this becomes a problem, though the effective range of the spin-traced 1-RDM may provide an indication. Computational studies suggest that for linear alkanes (*i.e.*, one-dimensional insulators) the effective range $|\mathbf{r} - \mathbf{r}'|$ over which $D_1(\mathbf{r};\mathbf{r}')$ is non-negligible is about 15–20 carbon atoms,[54] depending on drop tolerances, and we may judge that for larger systems extensivity violations may have important consequences. Lack of size-consistency is also a concern when breaking bonds, dissociating clusters, or comparing correlation energies between systems with different numbers of electrons.

In the present context, the way to insure extensivity is to reformulate the CSE so that the RDMCs and not the RDMs are the basic variables. One can always recover the RDMs from the cumulants, but only the cumulants satisfy connected equations that do not admit the possibility of mixing non-interacting subsystems. Connected equations are derived in Section 1.5. Before introducing that material, we first provide a general formulation of the $p$-RDMC for arbitrary $p$.

### 1.3.2 Cumulant formalism

Following Ziesche,[35,55] in order to develop the theory of cumulants for noncommuting creation and annihilation operators (as opposed to classical variables), we introduce field operators $f(\mathbf{x})$ and $f^\dagger(\mathbf{x})$ satisfying the anticommutation relations for a Grassmann field,

$$\big[f(\mathbf{x}),\ f(\mathbf{x}')\big]_+ = 0 \tag{1.18a}$$

$$\big[f(\mathbf{x}),\ f^\dagger(\mathbf{x}')\big]_+ = 0\ . \tag{1.18b}$$

These field operators are sometimes termed *probe variables* because they function as dummy placeholders in the formal differentiations that follow but do not appear in the final expressions for the cumulants, which are obtained formally in the limit that $f, f^\dagger \to 0$.

First, we define a functional $\mathcal{G}[f, f^\dagger]$ whose derivatives generate the RDMs. In terms of the usual field operators $\hat{\psi}(\mathbf{x})$ and $\hat{\psi}^\dagger(\mathbf{x}')$,

$$\hat{\psi}(\mathbf{x}) = \sum_k \phi_k(\mathbf{x})\ \hat{a}_k\ , \tag{1.19}$$

the RDM generating functional is[55]

$$\mathcal{G}[f, f^\dagger] = \left\langle \Psi \left| \hat{\mathcal{N}} \exp\left( \int d\mathbf{x}\ \big[f(\mathbf{x})\,\hat{\psi}^\dagger(\mathbf{x}) + f^\dagger(\mathbf{x})\,\hat{\psi}(\mathbf{x})\big] \right) \right| \Psi \right\rangle\ . \tag{1.20}$$

This is an analogue of the classical moments-generating functional discussed by Kubo.[39] Upon expanding the exponential as a power series, the operator $\hat{\mathcal{N}}$ acts to place each term in so-called normal order, in which all creation operators $\hat{\psi}^\dagger$ are to the left of all annihilation operators $\hat{\psi}$. By virtue of this ordering (and *only* by virtue of this ordering),

$$\begin{aligned}\mathcal{G}[f, f^\dagger] &= \left\langle \exp\left( \int d\mathbf{x}\ f(\mathbf{x})\,\hat{\psi}^\dagger(\mathbf{x}) \right)\ \exp\left( \int d\mathbf{x}'\ f^\dagger(\mathbf{x}')\,\hat{\psi}(\mathbf{x}') \right) \right\rangle \\ &= 1 + \mathcal{F}[f, f^\dagger]\ ,\end{aligned} \tag{1.21}$$

where $\langle \cdots \rangle = \langle \Psi | \cdots | \Psi \rangle$ and

$$\mathcal{F}[f, f^\dagger] = \sum_{p=1}^{\infty} \frac{1}{p!^2} \left\langle \int d\mathbf{x}_1 \cdots d\mathbf{x}_p \, d\mathbf{x}'_1 \cdots d\mathbf{x}'_p \; f(\mathbf{x}_1)\, \hat{\psi}^\dagger(\mathbf{x}_1) \cdots f(\mathbf{x}_p)\, \hat{\psi}^\dagger(\mathbf{x}_p) \right. \\ \left. \times\, f^\dagger(\mathbf{x}'_p)\, \hat{\psi}(\mathbf{x}'_p) \cdots f^\dagger(\mathbf{x}'_1)\, \hat{\psi}(\mathbf{x}'_1) \right\rangle . \tag{1.22}$$

The expectation value in Eq. (1.21) eliminates terms that do not conserve particle number, hence the two exponentials in Eq. (1.21) yield only a single summation in Eq. (1.22). The factor of $1/p!^2$ insures that tr $D_p = \binom{N}{p}$.

Formally, the logarithm $\ln \mathcal{G}$ provides a generating functional for the cumulants. That is, a formal expression for the $p$-RDMC is

$$\Delta_{p(1,\ldots,p;1',\ldots,p')} = \frac{1}{p!} \left( \lim_{f, f^\dagger \to 0} \frac{\delta^{2p}}{\delta f_{(1)}\, \delta f^\dagger_{(1')} \cdots \delta f_{(p)}\, \delta f^\dagger_{(p')}} \ln \mathcal{G} \right) . \tag{1.23}$$

(The normalization of the cumulants is more complicated that that of the RDMs, but some specific examples are given in Section 1.3.3.) Although ostensibly tedious, the above definition of $\Delta_p$ is operationally easy to use. In a formal expansion of $\ln \mathcal{G} = \ln(1 + \mathcal{F})$, the functional derivatives in Eq. (1.23) serve to select all terms consisting of exactly $p$ creation operators $\hat{\psi}^\dagger$ and exactly $p$ annihilation operators $\hat{\psi}$, while at the same time eliminating the integrals and replacing the dummy integration variables with particle coordinates $\mathbf{x}_1, \ldots, \mathbf{x}_p$ and $\mathbf{x}'_1, \ldots, \mathbf{x}'_p$.

As introduced above, the functional $\ln \mathcal{G}[f, f^\dagger]$ generates the cumulants as position-space kernels. As an alternative, Mazziotti[13,33] has introduced a generating functional for the expansion coefficients $\boldsymbol{\Delta}_{i_1,\ldots,i_p;j,\ldots,j_p}$ of $\Delta_p$ in a basis $\{\phi_k\}$ of orthonormal spin orbitals. Mazziotti's formalism can be obtained from the expressions above by expanding the Grassmann fields $f$ and $f^\dagger$ in this basis,

$$f(\mathbf{x}) = \sum_k J_k \; \phi_k(\mathbf{x}) \; . \tag{1.24}$$

The $J_k$ are the probe variables in this formulation (which Mazziotti[33] terms "Schwinger probes"). We mention also Kutzelnigg and Mukherjee's treatment of RDMCs,[28] which utilizes an antisymmetrized logarithm function, along with some special creation and annihilation operators, to generate the elements $\boldsymbol{\Delta}_{i_1,\ldots,i_p;j_1,\ldots,j_p}$.

Using either Eq. (1.23) or Mazziotti's adaptation of it, one may derive exact expression for the RDMs in terms of their cumulants. The first few such expressions are

$$
\begin{aligned}
D_1 &= \Delta_1 \ , && \text{(1.25a)}\\
D_2 &= \Delta_1^{\wedge 2} + \Delta_2 \ , && \text{(1.25b)}\\
D_3 &= \Delta_1^{\wedge 3} + 3\,\Delta_2 \wedge \Delta_1 + \Delta_3 \ , && \text{(1.25c)}\\
D_4 &= \Delta_1^{\wedge 4} + 6\,\Delta_2 \wedge \Delta_1^{\wedge 2} + 3\,\Delta_2^{\wedge 2} + 4\,\Delta_3 \wedge \Delta_1 + \Delta_4 \ , && \text{(1.25d)}\\
D_5 &= \Delta_1^{\wedge 5} + 10\,\Delta_2 \wedge \Delta_1^{\wedge 3} + 10\,\Delta_3 \wedge \Delta_1^{\wedge 2} + 5\,\Delta_4 \wedge \Delta_1 && \text{(1.25e)}\\
&\qquad + 15\,\Delta_1 \wedge \Delta_2^{\wedge 2} + 10\,\Delta_2 \wedge \Delta_3 \ .
\end{aligned}
$$

Here "$\wedge$" denotes an antisymmetrized product (*Grassmann product*[47,56])

$$
\begin{aligned}
&\big(\Delta_p \wedge \Delta_q\big)_{(1,\ldots,p+q;1',\ldots,(p+q)')}\\
&\qquad = \frac{1}{(p+q)!^2}\,\hat{\mathsf{P}}_{p+q}\,\hat{\mathsf{P}}'_{p+q}\Big[\Delta_{p(1,\ldots,p;1',\ldots,p')}\\
&\qquad\qquad \times \Delta_{q(p+1,\ldots,p+q;(p+1)',\ldots,(p+q)')}\Big] \ , \qquad \text{(1.26)}
\end{aligned}
$$

where $\hat{\mathsf{P}}'_{p+q}$ and $\hat{\mathsf{P}}_{p+q}$ indicate sums over signed permutations of the primed and unprimed coordinates, respectively [*cf.* Eq. (1.12)]. "Wedge" exponents appearing in Eqs. (1.25) are defined according to

$$
\Delta_p^{\wedge n} \overset{\text{def}}{=} \underbrace{\Delta_p \wedge \Delta_p \wedge \cdots \wedge \Delta_p}_{n \text{ factors}} \qquad \text{(1.27)}
$$

and should not be confused with matrix products such as $\Delta_1^n$, the matrix product of $n$ copies of $\Delta_1$.

The decomposition of $D_2$ in Eq. (1.25b) is sometimes called the Levy-Lieb partition of the 2-RDM.[57,58] Formulas essentially equivalent to Eqs. (1.25) were known long ago, in the context of time-dependent Green's functions,[59–61] but this formalism was rediscovered in the present context by Mazziotti.[33]

Implicit in Eqs. (1.25) are definitions of the cumulants in terms of the RDMs, for example,

$$
\begin{aligned}
\Delta_2 &= D_2 - D_1 \wedge D_1 \ , && \text{(1.28a)}\\
\Delta_3 &= D_3 - 2D_1^{\wedge 3} - 3D_1 \wedge D_2 \ , && \text{(1.28b)}\\
\Delta_4 &= D_4 + 13D_1 \wedge D_3 + 6D_1^{\wedge 2} \wedge D_2 - 4D_1 \wedge D_3 \ . && \text{(1.28c)}
\end{aligned}
$$

These equations *define* the RDMCs in terms of the RDMs, and do not depend upon the validity of perturbative expansions of the RDMs, although insofar as perturbation theory is applicable, $\Delta_p$ is precisely the sum of connected diagrams in the expansion of $D_p$.

The cumulant formulas in Eqs. (1.28) can be generated easily using a convenient mnemonic introduced by Harris.[62] To obtain the cumulant decomposition of $D_{p+1}$

from that of $D_p$, one sums—for each term in the $D_p$—all possible ways in which the particle number can be increased by one. Particle number can be increased either by replacing $\Delta_n$ with $\Delta_{n+1}$, or by incorporating an additional Grassmann product with $\Delta_1$. As an example, consider generating $D_3$ [Eq. (1.25c)] from $D_2$ [Eq. (1.25b)]. Given the first term in Eq. (1.25b), $\Delta_1 \wedge \Delta_1$, one can increase particle number in three ways, and from these one obtains $\Delta_2 \wedge \Delta_1 + \Delta_1 \wedge \Delta_2 + \Delta_1 \wedge \Delta_1 \wedge \Delta_1$. The second term in Eq. (1.25b), $\Delta_2$, affords $\Delta_3 + \Delta_2 \wedge \Delta_1$ upon increase in particle number. Together, these terms afford Eq. (1.25c).

This mnemonic emphasizes the combinatorial nature of the cumulants. For example, the term $3D_2 \wedge D_1$ in $D_3$ carries a coefficient that reflects the fact that there are three ways to obtain a three-particle distribution from one- and two-particle distributions, namely, $D_1 \wedge D_1 \wedge D_1$, $D_1 \wedge D_2$, and $D_2 \wedge D_1$. In contrast, the term $D_1^{\wedge 3}$ in $D_3$ has a coefficient of unity because there is only one way to combine one-particle distributions.

The combinatorial point of view is reminiscent of the classical cumulant formalism developed by Kubo,[39] and indeed the structure of Eqs. (1.25) and (1.28) is essentially the same as the equations that define the classical cumulants, up to the use of an antisymmetrized product in the present context. In further analogy to the classical cumulants, the $p$-RDMC is identically zero if simultaneous $p$-electron correlations are negligible. In that case, the $p$-RDM is precisely an antisymmetrized product of lower-order RDMs.

### 1.3.3 Extensivity

For a multiplicatively-separable wave function like the one in Eq. (1.12), the matrix elements of $\Delta_p$ vanish unless all indices correspond to the same subsystem.[28,32] Using the notation introduced previously, this means that $\boldsymbol{\Delta}_{j_1,\ldots,j_p;k_1,\ldots,k_p} = 0$ unless $\phi_m \in \mathcal{B}_{\mathrm{A}}$ for each index $m$ or else $\phi_m \in \mathcal{B}_{\mathrm{B}}$ for each $m$. This is the essential difference that allows for an extensive formulation of quantum mechanics in terms of the RDMCs but not in terms of the RDMs. From the standpoint of extensivity, the basic problem with the RDMs is the manner in which the exchange terms in their unconnected parts mix the coordinates corresponding to non-interacting subsystems. Such exchange terms are identified by the presence of a Grassmann product. Examining the cumulant decompositions of the RDMs in Eqs. (1.25), it is evident that any term containing a Grassmann product scales asymptotically ($N \to \infty$) like $N^n$, for some $n > 1$. For example, the Grassmann product

$$[\Delta_1 \wedge \Delta_1]_{(1,2;1',2')} = \frac{1}{2}\big[\Delta_{1(1;1')}\,\Delta_{1(2;2')} - \Delta_{1(1;2')}\,\Delta_{1(2;1')}\big] \tag{1.29}$$

appearing as part of $D_2$ has a trace given by

$$\mathrm{tr}\,\big(\Delta_1 \wedge \Delta_1\big) = N^2 - \mathrm{tr}\,(\Delta_1^2)\ . \tag{1.30}$$

As $N \to \infty$, tr $(\Delta_1 \wedge \Delta_1) \sim N^2$. One says that $\Delta_1 \wedge \Delta_1$ scales like $N^2$.

One convenient consequence of binomial normalization for the RDMs [Eq. (1.6)] is that when this convention is followed, extensive quantities such as $\Delta_p$ have traces proportional to $N$, while non-extensive quantities possess traces that scale as some higher power of $N$ (tr $D_p \sim N^p$, for example). Let us define a set of quantities

$$\tau_k \overset{\text{def}}{=} \frac{\text{tr}\left(\Delta_1^k\right)}{N} \tag{1.31}$$

that satisfy the property

$$1 = \tau_1 \geq \tau_2 \geq \tau_3 \geq \cdots \geq 0 \ , \tag{1.32}$$

which follows from the fact that all eigenvalues of $\Delta_1$ lie in the interval $[0,\, 1]$. Equation (1.32) is valid even for extended systems, where $N \to \infty$. In fact, without loss of generality one may assume that $\tau_k > 0$ for each $k$, since the $N$-electron wave function can always be expanded in terms of natural spin orbitals having strictly positive occupation numbers.[24] The limiting case in which $\tau_k = 1$ for all $k$ is obtained if and only if the two-electron interaction $\hat{g} \equiv 0$. In this case, the wave function is a single determine, $D_1$ is idempotent, and[45]

$$D_p = D_1^{\wedge p} \quad \text{(single determinant)} \ . \tag{1.33}$$

This form of $D_p$ implies that $\Delta_p \equiv 0$ for each $p > 1$, a reflection of the fact that an independent-electron wave function consists of one-electron subsystems coupled only by exchange.

Traces of the RDMCs can be expressed conveniently in terms of the $\tau_k$. For example,

$$\text{tr}\,\Delta_2 = \tfrac{1}{2}N(\tau_2 - 1) \tag{1.34}$$

and

$$\text{tr}\,\Delta_3 = \tfrac{1}{3}N\left(1 - 3\tau_2 + 2\tau_3\right) \ . \tag{1.35}$$

Given the inequalities in Eq. (1.32), these trace expressions make it clear that tr $\Delta_2 \sim N$ and tr $\Delta_3 \sim N$, even as $N \to \infty$, and furthermore they demonstrate that the normalization of the $p$-RDMC depends upon the system in question. (In particular, the traces depend upon how far $D_1$ deviates from idempotency.) A few absolute bounds can be derived, such as

$$-\tfrac{1}{2}N \leq \text{tr}\,\Delta_2 \leq 0 \ . \tag{1.36}$$

These inequalities do not exclude the possibility that $\Delta_2$ has both positive and negative eigenvalues, which is generally the case. Traces of $\Delta_2$ and $\Delta_3$ have been examined for some model problems by Kutzelnigg and Mukherjee.[28]

Partial traces of cumulants are also extensive, unlike those of the RDMs themselves. Starting from Eq. (1.25c), for example, one may show that

$$\mathrm{tr}_3\,\Delta_3 = -\tfrac{2}{3}\Delta_2 + \tfrac{1}{6}\left[\hat{\mathsf{P}}_2'\big(\Delta_1\Delta_2\big) + \hat{\mathsf{P}}_2\big(\Delta_2\Delta_1\big)\right] \;, \tag{1.37}$$

where the matrix products are defined, for example, as

$$(\boldsymbol{\Delta_1}\boldsymbol{\Delta_2})_{i_1,i_2;j_1,j_2} = \sum_k \boldsymbol{\Delta}_{i_1;k}\boldsymbol{\Delta}_{i_2,k;j_1,j_2} \;. \tag{1.38}$$

One may verify directly that tr $(\Delta_1\Delta_2) = N(\tau_3 - \tau_2)/2$ and therefore tr $(\Delta_1\Delta_2) \sim N$.

A word about notation is in order, regarding Eq. (1.37). Previously [*cf.* Eq. (1.26)], $\hat{\mathsf{P}}_n'$ and $\hat{\mathsf{P}}_n$ were defined to act upon primed and unprimed coordinates of $n$-electron kernels. Where tensors are involved, such as in Eq. (1.37), $\hat{\mathsf{P}}_n'$ represents signed permutations over the row indices, *i.e.*, the first set of indices) and $\hat{\mathsf{P}}_n$ denotes signed permutations over column indices. Thus, for example, when $\hat{\mathsf{P}}_2'$ acts on $\Delta_1\Delta_2$ in Eq. (1.37), this operation antisymmetrizes the indices $i_1$ and $i_2$ appearing in Eq. (1.38). The column indices ($j_1$ and $j_2$) of this product are already antisymmetric, having inherited this property from $\Delta_2$.

As noted above, tr $\Delta_n \sim N$ when binomial normalization is used for the RDMs, while non-extensive terms have traces that scale as higher powers of $N$. This is certainly a convenient means to recognize terms that are not extensive, but in some sense this trick overlooks the physical picture behind extensivity, which does not depend upon any particular normalization convention. Similarly, insofar as perturbation theory is applicable, the fact that the RDMCs scale as $N$ can be viewed as a consequence of the linked-cluster theorem,[63,64] but the deeper concept of extensivity does not depend upon the validity of perturbation theory. Mathematically, extensivity is a statement about connectivity in the sense of matrix products, as in Eq. (1.38). In Section 1.5, we introduce a nonperturbative diagram notation that emphasizes connectivity and extensivity, and demonstrates that $D_n$ (as opposed to $\Delta_n$) contains unconnected products, up to and including the product of $n$ unconnected one-electron diagrams.

Thus far we have discussed connectivity and extensivity in terms of the RDMs and RDMCs, but our ultimate goal is to apply these concepts to CSE(2). Replacing the RDMs in $\Omega_2$ with their cumulant decompositions elucidates the unconnected terms in CSE(2). Consider, as an example, the following term in $\Omega_{2(1,2;1',2')}$:

$$\begin{aligned}\hat{h}_{(1)}\,D_{2(1,2;1',2')} \\ = \hat{h}_{(1)}\Big[\Delta_{2(1,2;1',2')} + \tfrac{1}{2}\Delta_{1(1;1')}\,\Delta_{1(2;2')} - \tfrac{1}{2}\Delta_{1(1;2')}\,\Delta_{1(2;1')}\Big] \;. \end{aligned} \tag{1.39}$$

[This is the first term on the right side of Eq. (1.10), for the case $p = 2$.] The first term on the right in Eq. (1.39) is obviously connected, and we may deduce that the second term is unconnected because its trace equals $N^2\langle\hat{h}\rangle/2$. The third term, which constitutes a *transvection*[27,62] of $\Delta_1$ with itself, is actually connected, but differs from the second term by a coordinate permutation. If the second term is removed from CSE(2) then the third term ought to be removed as well, for otherwise we destroy the antisymmetry of $\Omega_2$. This example illustrates the complexity of formulating an extensive version of CSE(2). It is not enough to eliminate unconnected terms; on must eliminate their exchange counterparts as well.

### 1.3.4 Independence of the cumulants

Before deriving equations that determine the RDMCs, we ought to clarify precisely which are the RDMCs of interest. It is clear, from Eqs. (1.25a) and (1.25b), that $\Delta_1$ and $\Delta_2$ contain the same information as $D_2$ and can therefore be used to calculate expectation values $\langle\hat{W}\rangle$, where $\hat{W}$ is any symmetric two-electron operator of the form given in Eq. (1.1). Whereas the 2-RDM contains all of the information available from the 1-RDM, and affords the value of $\langle\hat{W}\rangle$ with no additional information, the 2-RDMC in general does not determine the 1-RDM,[43,65] so both $\Delta_1$ and $\Delta_2$ must be determined independently in order to calculate $\langle\hat{W}\rangle$. More generally, $\Delta_1, \ldots, \Delta_n$ are all independent quantities, whereas the RDMs $D_1, \ldots, D_n$ are related by the partial trace operation. The $n$-RDM determines all of the lower-order RDMs and lower-order RDMCs, but $\Delta_n$ alone is insufficient to specify *any* of the other cumulants, or any RDMs at all (save for the trivial $n = 1$ case).

A simple proof that $\Delta_1$ and $\Delta_2$ are independent proceeds as follows. First, observe that

$$\text{tr}_2\,\Delta_2 = \tfrac{1}{2}\left(\Delta_1^2 - \Delta_1\right)\ , \tag{1.40}$$

from which it follows that $\Delta_1$ and $\text{tr}_2\,\Delta_2$ share a common set of eigenvectors, namely, the natural spin orbitals. Let $\{n_k\}$ be the natural occupation numbers (eigenvalues of $\Delta_1$), and for each $n_k$, let $e_k$ be the eigenvalue of $\text{tr}_2\,\Delta_2$ associated with the same eigenvector. These two eigenvalues are related according to

$$e_k = \tfrac{1}{2}\,n_k(n_k - 1)\ , \tag{1.41}$$

or in other words

$$n_k = \tfrac{1}{2}\left(1 \pm \sqrt{1 + 8\,e_k}\right)\ . \tag{1.42}$$

Thus $n_k$ is a double-valued function of $e_k$, as depicted in Fig. 1.1. Strictly speaking, then, the eigenvalues of $\text{tr}_2\,\Delta_2$ do not determine those of $\Delta_1$, and consequently $\Delta_1$ cannot be determined from $\Delta_2$ alone.

That being said, in reality each eigenvalue of $\Delta_1$ will likely be near either 0 or 1, except in certain open-shell systems with significant multideterminant character. Excluding such cases, it may be possible that, given $\Delta_2$ (and thus the $e_k$), one can choose, for each $k$, one of the two solutions $n_k$ in Eq. (1.42), based upon whether the $k$th natural spin orbital is expected to be strongly or weakly occupied. (This could be determined by its expansion in Hartree-Fock orbitals.) Suppose that either

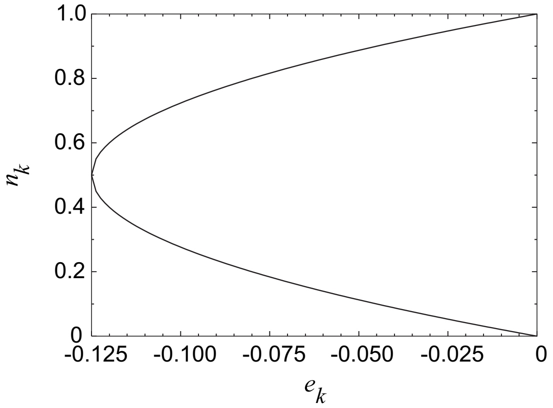


**Fig. 1.1** An eigenvalue $n_k$ of $\Delta_1$ as a (double-valued) function of the corresponding eigenvalue $e_k$ of tr$_2$ $\Delta_2$.

$n_k = \varepsilon$ or $n_k = 1 - \varepsilon$, where $\varepsilon$ is small. Upon calculating $e_k$ corresponding to each, and substituting this back into Eq. (1.42), one obtains in either case a choice between solutions $n_k = 1 - \varepsilon + O(\varepsilon^2)$ and $n_k = \varepsilon + O(\varepsilon^2)$. So long as $\varepsilon^2 \ll \varepsilon$, and assuming that one can ascertain which natural spin orbitals are strongly occupied, $\Delta_2$ effectively does determine $\Delta_1$. In such cases, $\langle \hat{W} \rangle$ can be determined from $\Delta_2$ alone.

## 1.4 DIAGRAMMATIC REPRESENTATIONS

As outlined above, our task is to eliminate from CSE(2) both the unconnected terms *and* their exchange counterparts. These are readily identified using diagrammatic representations of $\Omega_1$ and $\Omega_2$ that we introduce in this section. The diagrams are not strictly necessary, but are quite convenient and (in the authors' opinion) easier to check for mistakes than lengthy algebraic formulas. In addition, certain reconstruction functionals for the 3- and 4-RDMs have been derived using diagrammatic many-body perturbation theory,[7,8,11] and a diagrammatic representation for CSE(2) clarifies the role of this equation in improving approximate reconstruction functionals (see Section 1.5.3). Our diagram conventions are conceived with this purpose in mind, and are unrelated to the CSE diagrams introduced by Mukherjee and Kutzelnigg.[30,31]

The basic diagram elements representing $D_1 \equiv \Delta_1$, $\hat{h}$ $\hat{g}$ and $\Delta_p$ (for $p \geq 2$) are illustrated in Fig. 1.2. Recall that CSE($p$) is given by the equation $\Omega_p \equiv 0$, where the $\Omega_p$ is the $p$-electron kernel defined in Eq. (1.10). The terms in this kernel consist of $\hat{h}$ and $\hat{g}$ acting on RDMs, followed in some cases by a trace over one or two coordinate indices. Upon replacing the RDMs with their cumulant expansions [Eqs. (1.28)], we construct a diagrammatic representation of each term by connecting

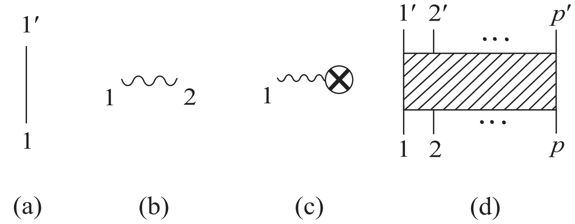
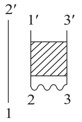


**Fig. 1.2** Basic diagram elements used in this work: (a) $D_1(1;1')$; (b) $\hat{g}(1,2)$; (c) $\hat{h}(1)$; and (d) $\Delta_p(1,\ldots,p;1',\ldots,p')$, for $p \geq 2$.

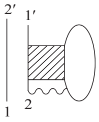
operator diagrams to cumulant diagrams, at the coordinates on which the operators act. For instance,



$$= \hat{g}(2,3)\,\Delta_1(1;2')\;\Delta_2(2,3;1',3') \tag{1.43}$$

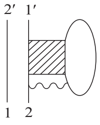
is obtained by attaching a $\hat{g}$ diagram at the lower endpoints of a $\Delta_2(2,3;1',3')$ diagram, since according to Fig. 1.2(d) these endpoints represent coordinates $\mathbf{x}_2$ and $\mathbf{x}_3$. A factor of $\Delta_1(1;2')$ is present, as indicated, but because $\hat{g}(2,3)$ operates on neither $\mathbf{x}_1$ nor $\mathbf{x}_2'$, this part of the diagram is not connected to the rest. Inspection of either the diagram of the algebra in Eq. (1.43) reveals that this term is unconnected.

A trace over coordinate $\mathbf{x}_n$ is indicated by connecting the line labeled $n$ to the line labeled $n'$. The labels $n$ and $n'$ are then deleted, since these coordinates become a single dummy integration variable. Diagrammatically, this creates a loop in the case that both $\mathbf{x}_n$ and $\mathbf{x}_n'$ are arguments of the same cumulant. As an example, we apply $\text{tr}_3$ to Eq. (1.43) to obtain



$$= \Delta_1(1;2')\,\text{tr}_3\left\{\hat{g}(2,3)\,\Delta_2(2,3;1',3')\right\}\,. \tag{1.44}$$

If, on the other hand, $\mathbf{x}_n$ and $\mathbf{x}_n'$ are arguments of different cumulants, then a trace over $\mathbf{x}_n$ serves to connect two cumulant diagrams:

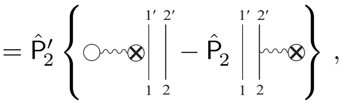


$$= \Delta_1(1;2')\,\text{tr}_{3,4}\left\{\hat{g}(3,4)\,\Delta_1(2;3')\,\Delta_2(3,4;1',4')\right\}\,. \tag{1.45}$$

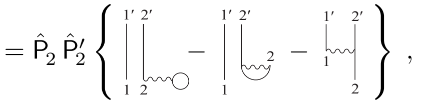
Note carefully the subtle difference between this diagram and the previous one, at the position labeled “2”. These two examples illustrate that *internal* operator vertices (those not appearing at the endpoint of a cumulant line) are each associated with a coordinate integration, whereas a vertex that appears at the endpoint of a cumulant line does not imply an integration. Thus, in Eq. (1.45), both ends of the $\hat{g}$ diagram are internal vertices, reflecting the fact that both arguments of $\hat{g}$ are integration variables. In Eq. (1.44), only one argument of $\hat{g}$ is an integration variable and thus the $\hat{g}$ diagram has one internal and one external vertex, the latter associated with $\mathbf{x}_2$.

In close analogy to diagrammatic perturbation theory (although our diagrams are not perturbative), we have transformed the problem of generating terms in $\Omega_p$ into a problem of generating topologically distinct diagrams, which makes it relatively easy to incorporate symmetries such as $\hat{g}(j,k) = \hat{g}(k,j)$ that reduce the number of terms in $\Omega_p$. The nontrivial terms in $\Omega_1$ and $\Omega_2$ that involve only the one-electron cumulant are

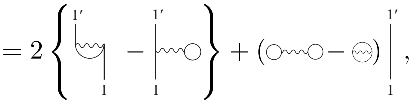
$$6\,\mathrm{tr}_3\left\{\hat{h}(3)\,\Delta_1^{\wedge 3}(1,2,3;1',2',3')\right\} = \tag{1.46}$$



$$6\,\mathrm{tr}_3\left\{\left[\hat{g}(1,3)+\hat{g}(2,3)\right]\Delta_1^{\wedge 3}(1,2,3;1',2',3')\right\} \tag{1.47}$$

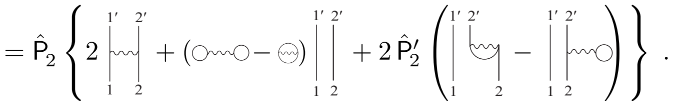


$$6\,\mathrm{tr}_{2,3}\left\{\hat{g}(2,3)\,\Delta_1^{\wedge 3}(1,2,3;1',2',3')\right\} = \tag{1.48}$$



and

$$24\,\mathrm{tr}_{3,4}\left\{\hat{g}(3,4)\,\Delta_1^{\wedge 4}(1,2,3,4;1',2',3',4')\right\} \tag{1.49}$$



These expressions are highly compact compared to brute-force expansions of the Grassmann products $\Delta_1^{\wedge 3}$ and $\Delta_1^{\wedge 4}$. For example, $\Delta_1^{\wedge 4}$ ostensibly contains $4!^2 = 576$ terms, as compared to the 14 terms that appear in Eq. (1.49) if one writes out all permutations.

Certain diagrams in the expressions above have no coordinate dependence, and are related to the eigenvalue $w$ in Eq. (1.2). Let us decompose $w = w_1 + w_2$ into a one-electron contribution

$$w_1 = N\langle\hat{h}\rangle \tag{1.50}$$

and a two-electron contribution

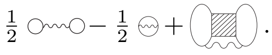
$$w_2 = \binom{N}{2}\langle\hat{g}\rangle\ . \tag{1.51}$$

with $\langle \hat{h} \rangle = \mathrm{tr}\,(\hat{h}\, D_1)$ and $\langle \hat{g} \rangle = \mathrm{tr}\,(\hat{g}\, D_2)$. These equations are expressed diagrammatically as

$$w_1 = \mathrm{tr}\left\{\hat{h}(1)\, \Delta_1(1;1')\right\} = \tag{1.52}$$

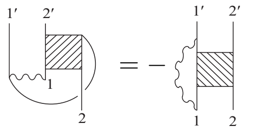
and

$$w_2 = \mathrm{tr}\left\{\hat{g}(1,2)\, D_2(1,2;1',2')\right\} = \tag{1.53}$$



When $w$ is the electronic energy, the first two terms on the right side of Eq. (1.53) are the Coulomb and exchange energies, respectively, while the third term defines what we term the *cumulant correlation energy*. The cumulant decomposition of $D_2$ thus provides universal, extensive definitions for the exchange and correlation energies, and these definitions do not depend upon any independent-electron (Hartree-Fock or Kohn-Sham) reference state. According to this definition, the (exact) Coulomb and exchange energies are available from the (exact) 1-RDM, while the cumulant correlation energy requires the 2-RDM.

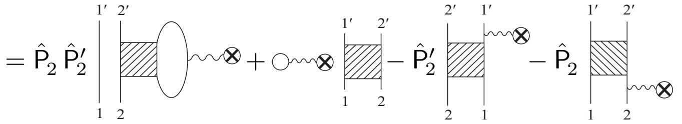
For expressions involving higher-order cumulants, one can utilize the antisymmetry of $\Delta_p$ to reduce the number of terms. For example, the identity



(1.54)

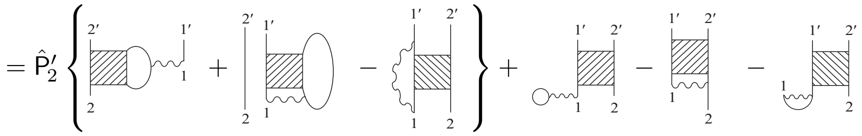
is obtained by exchanging the lines entering the top of $\Delta_2$, which corresponds to a permutation of the primed coordinates in $\Delta_2$. After gaining some facility with the diagrams, one can write down the remaining terms in $\Omega_2$:

$$9\,\mathrm{tr}_3\left\{\hat{h}(3)\,\big(\Delta_1 \wedge \Delta_2\big)(1,2,3;1',2',3')\right\}$$



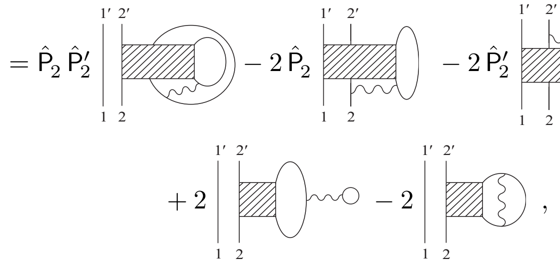
, (1.55)

$$9\,\mathrm{tr}_3\left\{\hat{g}(1,3)\,\big(\Delta_1 \wedge \Delta_2\big)(1,2,3;1',2',3')\right\}$$



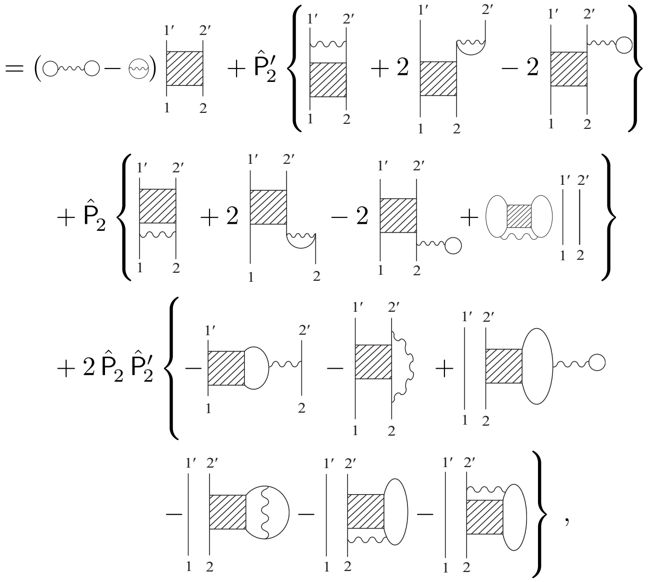
, (1.56)

$$16\,\mathrm{tr}_{3,4}\left\{\hat{g}(3,4)\left(\Delta_1\wedge\Delta_3\right)(1,2,3,4;1',2',3',4')\right\}$$



(1.57)

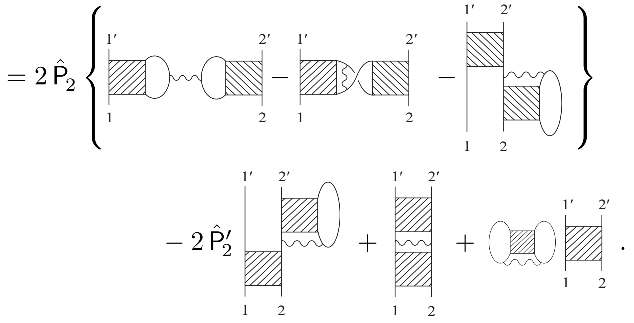
$$72\,\mathrm{tr}_{3,4}\left\{\hat{g}(3,4)\left(\Delta_1^{\wedge 2}\wedge\Delta_2\right)(1,2,3,4;1',2',3',4')\right\}$$



(1.58)

and

$$18\,\mathrm{tr}_{3,4}\left\{\hat{g}(3,4)\,\Delta_2^{\wedge 2}(1,2,3,4;1',2',3',4')\right\}$$



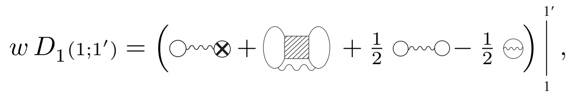
(1.59)

## 1.5 THE CONNECTED EQUATIONS

Recall that the equation CSE($p$) is written as $\Omega_{p\,(1,\ldots,p;1',\ldots,p')} \equiv 0$, where $\Omega_p$ is the $p$th-order energy density matrix. Yasuda[11] has introduced a generating functional for the energy density matrices and used this functional to demonstrate that $\Omega_p = \Omega_p^{\mathsf{C}} + \Omega_p^{\mathsf{U}}$ can be decomposed into a connected part $\Omega_p^{\mathsf{C}}$ and an unconnected part $\Omega_p^{\mathsf{U}}$. The diagrammatic technique introduced in the previous section brings this to the forefront, and in this section we use diagrammatic representations of $\Omega_1$ and $\Omega_2$ to formulate connected versions of CSE(1) and CSE(2). Whereas CSE(1) is necessarily satisfied if CSE(2) is satisfied (since the former is merely a partial trace of the latter[47]), the connected versions of CSE(1) and CSE(2) are independent conditions on the 1- and 2-RDMCs, which must be satisfied simultaneously.

### 1.5.1 Cancellation of unconnected terms

Clearly $\Omega_1$, as defined in Eq. (1.10), contains unconnected terms, including for example

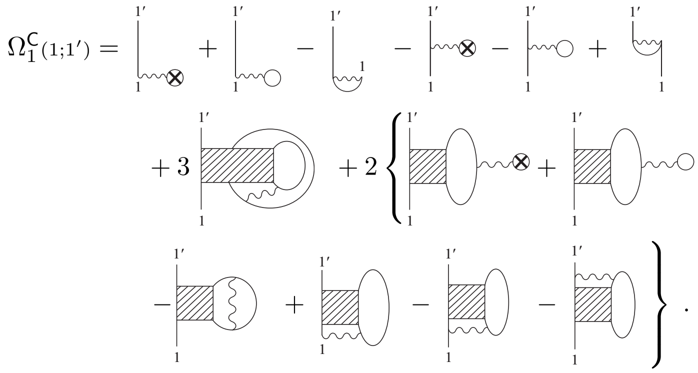


(1.60)

but these terms cancel exactly and $\Omega_1^{\mathsf{U}} \equiv 0$. Since an approximate solution of CSE(1) may not lead to exact cancellation of the unconnected terms, instead of solving the equation $\Omega_1 \equiv 0$, one ought to solve the manifestly extensive equation

$$\Omega_1^{\mathsf{C}} \equiv 0 \; . \tag{1.61}$$

The connected part of $\Omega_1$ is found to be



(1.62)

Since the unconnected terms cancel exactly, Eq. (1.61) is equivalent, in a necessary and sufficient sense, to CSE(1). Following Kutzelnigg and Mukherjee[29–31] we refer to Eq. (1.61) as the first-order *irreducible* contracted Schrödinger equation, ICSE(1). To obtain an equation that is equivalent, within a finite basis set, to our ICSE($p$), one must solve the Kutzelnigg-Mukherjee version[30] of ICSE($p$) simultaneously with its adjoint equation, whereas our version of ICSE($p$) is equal to its own adjoint, thus insuring that its solution $\Delta_p$ is self-adjoint.

Neither CSE(1) nor ICSE(1) is equivalent to the original Hilbert-space eigenvalue equation; for that we need CSE(2). The unconnected part of $\Omega_2$ is[11]

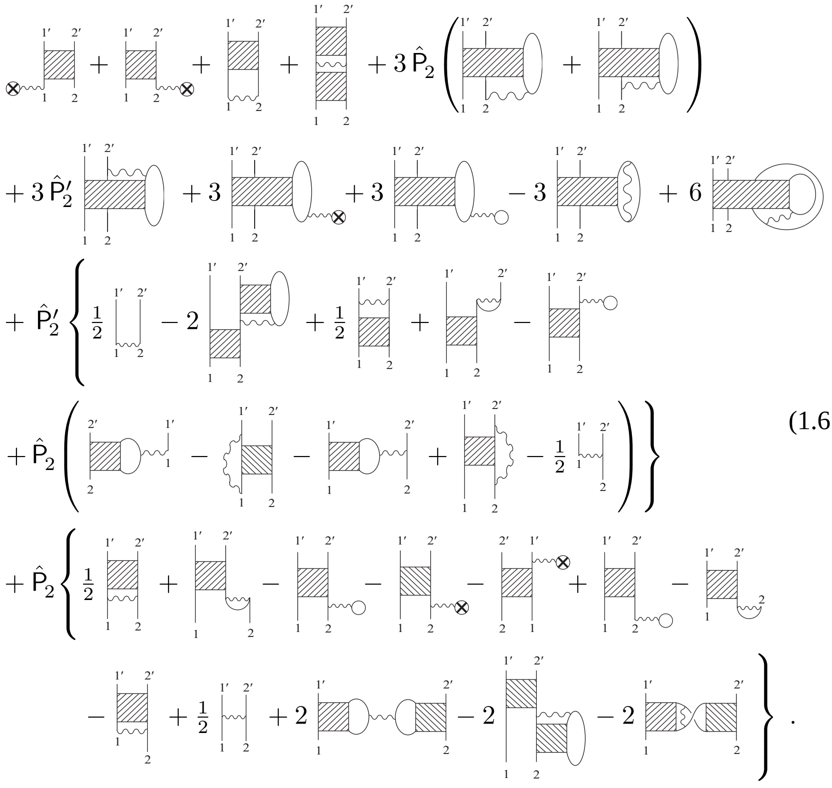
$$\Omega_2^{\mathsf{U}} = D_1 \wedge \Omega_1 = D_1 \wedge \Omega_1^{\mathsf{C}} \; . \tag{1.63}$$

This relationship can be verified directly using the expressions in the previous section. Thus, if $D_1$ satisfies CSE(1)—a necessary condition if $D_2$ is to satisfy CSE(2)—then $\Omega_2^{\mathsf{U}} = 0$ and we obtain the extensive equation

$$\Omega_2^{\mathsf{C}} \equiv 0 \; , \tag{1.64}$$

which we call ICSE(2). Carrying out the cancellation is relatively easy using diagrams, and one obtains

$\Omega^{\mathsf{C}}_{2(1,2;1',2')} =$

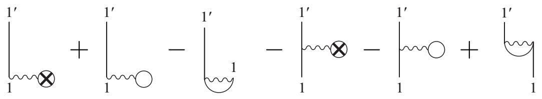


(1.65)

Including permutations, this expression for $\Omega_2^{\mathsf{C}}$ contains 68 terms, a significant reduction as compared to the unsimplified Grassmann products.

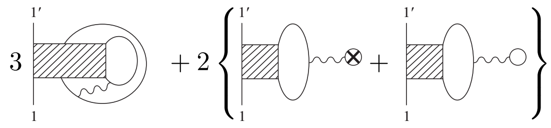
Equations (1.62) and (1.65), expressed in diagrammatic notation, are the only forms of ICSE(1) and ICSE(2) that appear in our original publication of the connected equations,[43] although a short time later a connected, algebraic version of CSE(2) was published by Nooijen and co-workers.[44] Here, we translate our diagrammatic versions equations into algebraic ones, using the diagram rules introduced in Section 1.4. For pedagogical purposes, and owing to the complexity of the result, we break up Eqs. (1.62) and (1.65) line-by-line, and present each line as a separate algebraic expression. In addition, certain obvious factorizations are bypassed in the algebraic formulation that follows, in order that diagrams on the left side of the equality match up with algebraic expressions on the right side term-by-term and in the same order. This facilitates comparison between the diagrammatic and the algebraic equations.

The algebraic form of $\Omega_1^{\mathsf{C}}$ is contained in the equations



(1.66a)

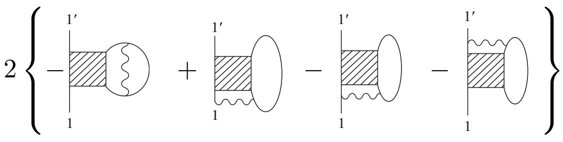
$$= \hat{h}(1)\,\Delta_1(1;1') + \mathrm{tr}_2\left\{\hat{g}(1,2)\left[\Delta_1(1;1')\,\Delta_1(2;2') - \Delta_1(1;2')\,\Delta_1(2;1')\right]\right\}$$
$$- \mathrm{tr}_2\left[\hat{h}(2)\,\Delta_1(1;2')\,\Delta_1(2;1')\right]$$
$$- \mathrm{tr}_{2,3}\left\{\hat{g}(2,3)\left[\Delta_1(1;2')\,\Delta_1(2;1')\,\Delta_1(3;3') - \Delta_1(1;2')\,\Delta_1(2;3')\,\Delta_1(3;1')\right]\right\}\,,$$



(1.66b)

$$= 3\,\mathrm{tr}_{2,3}\left[\hat{g}(2,3)\,\Delta_3(1,2,3;1',2',3')\right] + 2\,\mathrm{tr}_2\left[\hat{h}(2)\,\Delta_2(1,2;1',2')\right]$$
$$+ 2\,\mathrm{tr}_{2,3}\left[\hat{g}(2,3)\,\Delta_2(1,2;1',2')\,\Delta_1(3;3')\right]\,,$$

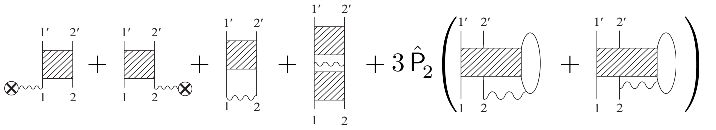
and



(1.66c)

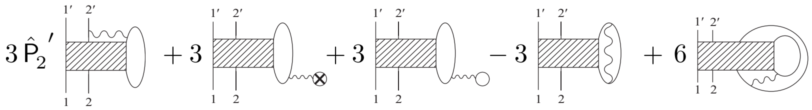
$$= -2\,\mathrm{tr}_{2,3}\left[\hat{g}(2,3)\,\Delta_2(1,2;1',3')\,\Delta_1(3;2')\right] + 2\,\mathrm{tr}_2\left[\hat{g}(1,2)\,\Delta_2(1,2;1',2')\right]$$
$$- 2\,\mathrm{tr}_{2,3}\left[\hat{g}(2,3)\,\Delta_2(2,3;1',2')\,\Delta_1(1;2')\right] - 2\,\mathrm{tr}_{2,3}\left[\hat{g}(2,3)\,\Delta_2(1,3;2',3')\,\Delta_1(2;1')\right]\,.$$

The kernel $\Omega_2^{\mathsf{C}}(1;1')$ is equal to the sum of the terms given in Eqs. (1.66a)–(1.66c). The various terms in ICSE(2) are

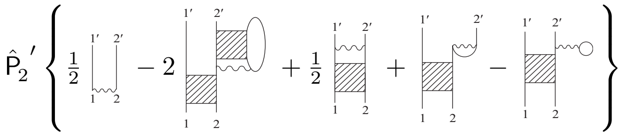


(1.67a)

$$= \left[\hat h(1) + \hat h(2) + \hat g(1,2)\right] \Delta_2(1,2;1',2') + \mathrm{tr}_{3,4}\left[\hat g(3,4)\, \Delta_2(1,2;3',4')\, \Delta_2(3,4;1',2')\right]$$
$$+ 3\,\hat{\mathsf{P}}_2 \Big\{ \mathrm{tr}_3 \left[\hat g(2,3)\, \Delta_3(1,2,3;1',2',3')\right] + \mathrm{tr}_{3,4}\left[\hat g(3,4)\, \Delta_3(1,3,4;1',2',4')\, \Delta_1(2;3')\right] \Big\} \;,$$

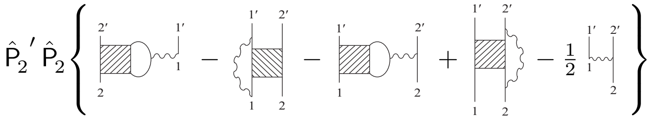


$$= 3\,\hat{\mathsf{P}}_2{}' \mathrm{tr}_{3,4} \left[\hat g(3,4)\, \Delta_3(1,2,3;1',4',3')\, \Delta_1(4;2')\right] + 3\,\mathrm{tr}_3 \left[\hat h(3)\, \Delta_3(1,2,3;1',2',3')\right]$$
$$+ 3\,\mathrm{tr}_{3,4} \left[\hat g(3,4)\, \Delta_3(1,2,3;1',2',3')\, \Delta_1(4;4')\right]$$
$$- 3\,\mathrm{tr}_{3,4} \left[\hat g(3,4)\, \Delta_3(1,2,3;1',2',4')\, \Delta_1(4;3')\right] \qquad (1.67b)$$
$$+ 6\,\mathrm{tr}_{3,4} \left[\hat g(3,4)\, \Delta_3(1,2,3,4;1',2',3',4')\right] \;,$$

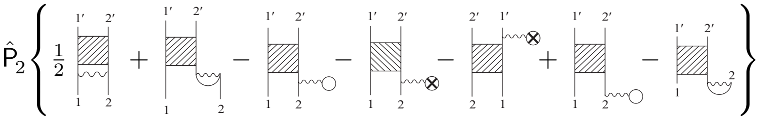


(1.67c)

$$= \hat{\mathsf{P}}_2{}' \Big\{ \tfrac{1}{2}\, \hat g(1,2)\, \Delta_1(1;1')\, \Delta_1(2;2') - 2\,\mathrm{tr}_{3,4} \left[\hat g(3,4)\, \Delta_2(1,2;1',3')\, \Delta_2(3,4;2',4')\right]$$
$$+ \tfrac{1}{2}\,\mathrm{tr}_{3,4} \left[\hat g(3,4)\, \Delta_2(1,2;3',4')\, \Delta_1(3;1')\, \Delta_1(4;2')\right]$$
$$+ \mathrm{tr}_{3,4} \left[\hat g(3,4)\, \Delta_2(1,2;1',3') \Big(\Delta_1(3;4')\, \Delta_1(4;2') - \Delta_1(3;2')\, \Delta_1(4;4')\Big)\right] \Big\} \;,$$

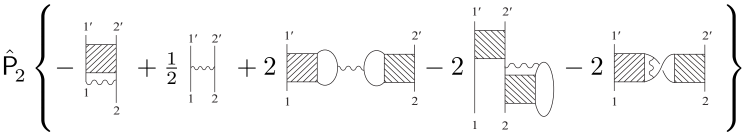


$$= \hat{\mathsf{P}}_2{}' \, \hat{\mathsf{P}}_2 \Big\{ \mathrm{tr}_3 \left[ \hat{g}(1,3)\, \Delta_2(2,3;2',3')\, \Delta_1(1;2') \right] - \mathrm{tr}_3 \left[ \hat{g}(1,3)\, \Delta_2(1,2;3',2')\, \Delta_1(3;1') \right]$$
$$- \mathrm{tr}_{3,4} \left[ \hat{g}(3,4)\, \Delta_2(1,3;1',3')\, \Delta_1(2;4')\, \Delta_1(4;2') \right]$$
$$+ \mathrm{tr}_{3,4} \left[ \hat{g}(3,4)\, \Delta_2(1,3;1',4')\, \Delta_1(2;3')\, \Delta_1(4;2') \right] \qquad (1.67d)$$
$$- \tfrac{1}{2}\, \mathrm{tr}_3 \left[ \Delta_1(1;1')\, \Delta_1(2;3')\, \Delta_1(3;2') \right] \Big\} \,,$$



$$= \hat{\mathsf{P}}_2 \Big\{ \tfrac{1}{2}\, \mathrm{tr}_{3,4} \left[ \hat{g}(3,4)\, \Delta_2(1,2;3',4')\, \Delta_1(3;1')\, \Delta_1(4;2') \right] \qquad (1.67e)$$
$$+ \mathrm{tr}_{3,4} \left[ \hat{g}(3,4)\, \Delta_2(1,3;1',2') \Big( \Delta_1(4;3')\, \Delta_1(2,4') - \Delta_1(2;3')\, \Delta_1(4;4') \Big) \right]$$
$$- \mathrm{tr}_3 \left[ \hat{h}(3)\, \Delta_2(1,3;1',2')\, \Delta_1(2;3') \right] - \mathrm{tr}_3 \left[ \hat{h}(3)\, \Delta_2(1,2;1',3')\, \Delta_1(3;2') \right]$$
$$- \mathrm{tr}_3 \left[ \hat{g}(2,3)\, \Delta_2(1,3;1',2')\, \Delta_1(2;3') \right] \Big\} \,,$$

and



$$= \hat{\mathsf{P}}_2 \Big\{ -\mathrm{tr}_3 \left[ \hat{g}(1,3)\, \Delta_2(1,3;1',2')\, \Delta_1(2;3') \right]$$
$$+ \tfrac{1}{2} \mathrm{tr}_{3,4} \left[ \hat{g}(3,4)\, \Delta_1(1;3')\, \Delta_1(2;4')\, \Delta_1(3;1')\, \Delta_1(4;2') \right] \qquad (1.67f)$$
$$+ 2\, \mathrm{tr}_{3,4} \left[ \hat{g}(3,4)\, \Delta_2(1,3;1',3')\, \Delta_2(4,2;4',2') \right]$$
$$- 2\, \mathrm{tr}_{3,4} \left[ \hat{g}(3,4)\, \Delta_2(1,3;1',2')\, \Delta_2(2,4;3',4') \right]$$
$$- 2\, \mathrm{tr}_{3,4} \left[ \hat{g}(3,4)\, \Delta_2(1,3;1',4')\, \Delta_2(4,2;3',2') \right] \Big\} \,.$$

The kernel $\Omega_2^{\mathsf{C}}(1,2;1',2')$ is equal to the sum of the terms given in Eqs. (1.67a)–(1.67f).

### 1.5.2 Discussion of the connected equations

Perhaps the most striking feature of ICSE(1) and ICSE(2) is the absence of the eigenvalue $w$ in these equations. In hindsight its disappearance should not be surprising, since $w$ appears in $\Omega_p$ as the product $wD_p$. The observable $w$ scales as $N$, as does the connected part of $D_p$, hence no part of $wD_p$ exhibits correct scaling, and this entire term must cancel with some other part of CSE($p$). (This is analogous to the fact that the coupled-cluster amplitude equations, which are extensive, contain the cluster amplitudes but not the electronic energy.) Certainly, $w$ is specified *implicitly* in ICSE(1) and ICSE(2), insofar as the cumulants $\Delta_1$ and $\Delta_2$ together determine $D_2$ and thus also determine $w = \text{tr}\,(\hat{W}_2\, D_2)$. The absence of $w$ in ICSE($p$) has important consequences, to which we shall return later in this section.

In deriving ICSE(1) and ICSE(2) from the corresponding CSEs, we have merely identified and removed terms that cancel exactly; as such, these two connected equations, when solved simultaneously, are entirely equivalent to CSE(2) and thus equivalent to the original Hilbert-space eigenvalue equation (Schrödinger equation), provided that appropriate $N$-representability constraints are enforced. Since necessary and sufficient $N$-representability constraints are not known, one must in practice contend with an infinite number of spurious solutions to these equations. Recent calculations[7,9,34,66] in which CSE(2) is solved starting from an $N$-representable (actually, Hartree-Fock) 2-RDM indicate that, for ground states, the solution usually converges to a 2-RDM that is nearly consistent with the necessary $P$-, $Q$-, and $G$-conditions[24,66,67] for $N$-representability. (These conditions demand that the two-particle density matrix, the two-hole density matrix, and the particle-hole density matrix, respectively, be positive semi-definite, and by “nearly consistent” we mean that any negative eigenvalues are small in magnitude.)

Even given a hypothetical set of necessary and sufficient $N$-representability constraints, however, the solution of CSE(2) is only unique provided that the eigenvalue $w$ is specified and fixed. Because $w$ does not appear in the ICSEs, a unique solution of ICSE(1) and ICSE(2) is obtained only by simultaneous solution of these equations subject not only to $N$-representability constraints but also subject to the constraint that $w = \text{tr}\,(\hat{W}_2\, D_2)$ remains fixed. For auxiliary constraint equations, such as the reduced eigenvalue equation for the operator $\hat{S}^2$, one would know the target expectation value $\langle \hat{S}^2 \rangle$ in advance, and could therefore constrain $\langle \hat{S}^2 \rangle = \text{tr}\,(\hat{S}_2^2\, D_2)$. In the basic equations of our theory, however, $\hat{W}$ is an electronic Hamiltonian and such a constraint would require us to know the electronic energy in advance. Foregoing the energy constraint, ICSE(1) and ICSE(2) possess $N$-representable solutions corresponding to the ground state, the excited states, and also all superposition states that can be formed from degenerate eigenfunctions of $\hat{W}$. This is again analogous to coupled-cluster theory, whose connected working equations do not contain the electronic energy explicitly, and have solutions corresponding to both ground and excited electronic states;[68] the ground-state solution is selected by means of the initial guess. Compared to CSE(2), the absence of the electronic energy in the ICSEs is not a serious disadvantage, since in the former case the energy is not known *a priori* and therefore $w$ appearing in CSE(2) must be iteratively updated during the course of achieving a self-consistent solution.

Before discussing further how ICSE(1) and ICSE(2) can be solved, let us first discuss the solution of CSE(2). For $w \neq 0$, CSE(2) may be written

$$D_2 = w^{-1} F_w[D_2, D_3, D_4] \,, \tag{1.68}$$

where the functional $F_w \equiv \Omega_2 + w D_2$ [*cf*. Eq. (1.10)]. Assuming that one posesses approximate reconstruction functionals $D_3[D_2]$ and $D_4[D_2]$, Eq. (1.68) can be solved for $D_2$ by one of two means. The first option is to substitute the reconstruction functionals directly into $F_w$, effectively making $F_w$ a functional of $D_2$ only. Upon expanding Eq. (1.68) in a finite basis set, this leads to a closed set of nonlinear equations for the tensor elements of $D_2$, and these equations can be solved, for example, by a Newton-Raphson procedure.[7,9,11] Alternatively, Eq. (1.68) can be solved by self-consistent iteration, employing the reconstruction functionals at each iteration to generate updated 3- and 4-RDMs from the current 2-RDM, and using the current 2-RDM to estimate $w$. Several algorithms for carrying out this iteration scheme have been described.[1,2,6,14]

It does not appear that the ICSEs can be solved by self-consistent iteration, however. In Eq. (1.68), CSE(2) is expressed in a form that affords the 2-RDM as an *explicit* functional of the 2-, 3-, and 4-RDMs, but no analogous formulation of ICSE(1) or ICSE(2) is possible, since the 1- and 2-RDMCs appearing in these equations are always acted upon by $\hat{h}$ or $\hat{g}$ [*cf*. Eqs. (1.66) and (1.67)]. Thus, the ICSEs are *implicit* equations for the cumulants.

Using cumulant reconstruction functionals $\Delta_3[\Delta_1, \Delta_2]$ and $\Delta_4[\Delta_1, \Delta_2]$, one can certainly derive closed, nonlinear equations for the elements of $\Delta_1$ and $\Delta_2$, which could be solved using an iterative procedure that does not exploit the reconstruction functionals at each iteration. Of the RDM reconstruction functionals derived to date, several[7,8,11] utilize the cumulant decompositions in Eqs. (1.25c) and (1.25d) to obtain the unconnected portions of $D_3$ and $D_4$ exactly (in terms of the lower-order RDMs), then use many-body perturbation theory to estimate the connected parts $\Delta_3$ and $\Delta_4$ in terms of $\Delta_1$ and $\Delta_2$, the latter essentially serving as a renormalized pair interaction. Reconstruction functionals of this type are equally useful in solving ICSE(1) and ICSE(2), but the reconstruction functionals introduced by Valdemoro and coworkers[25,26] cannot be used to solve the ICSEs because they contain no connected terms in $D_3$ or $D_4$ (and thus no contributions to $\Delta_3$ or $\Delta_4$).

### 1.5.3 Reconstruction and solution of the reduced equations

Next we present some observations concerning the connection between the reconstruction process and the iterative solution of either CSE($p$) or ICSE($p$). The perturbative reconstruction functionals mentioned above each constitutes a finite-order ladder-type approximation to the 3- and 4-RDMCs;[46,69] examples of the lowest-order corrections of this type are shown in Fig. 1.3. The hatched squares in these diagrams

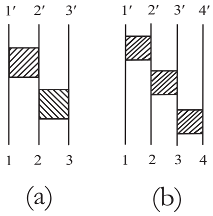


**Fig. 1.3** Lowest order connected corrections to (a) $\Delta_3$ and (b) $\Delta_4$, within a renormalized ladder-type approximation.

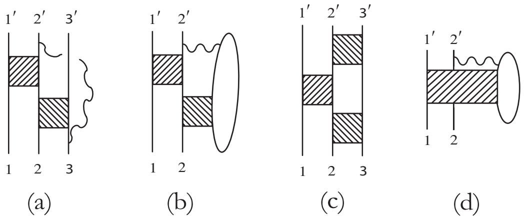


**Fig. 1.4** Diagrams illustrating the connection between reconstruction and solution of the CSEs or ICSEs. See the text for an explanation.

can be thought of as arising from the 2-RDM, which serves as an effective pair interaction in for a form of many-body perturbation theory. Ordinarily, ladder-type perturbation expansions neglect three-electron (and higher) correlations, even when extended to infinite order in the effective pair interaction,[46,69] but iterative solution of the CSEs (or ICSEs) helps to build these correlations back into the cumulants. This becomes clear upon examination of the diagrammatic representations of these equations, together with diagrammatic representations of the reconstruction functionals.

In Fig. 1.4(a) we show a typical diagram in the expansion of $\Delta_3$ that cannot be incorporated into any ladder-type diagram because it involves simultaneous correlation between three particles.[69] As it appears in CSE(2) and ICSE(2), however, $\Delta_3$ is always traced over coordinate $\mathbf{x}_3$, and in Fig. 1.4(b) we show the effect of $\mathrm{tr}_3$ on the diagram in 1.4(a). Diagram 1.4(b) *is* included in the partial trace of a *third*-order ladder-type diagram, namely the one shown in Fig. 1.4(c). Thus the presence of $\mathrm{tr}_3$ in the two-particle equations allows one to incorporate three- and higher-body effects that would not otherwise be present in a ladder approximation for the three- and four-electron cumulants.

Actually three-particle correlations such as that in Fig. 1.4(a) are introduced by the CSEs and ICSEs, even within a second-order ladder approximation. To understand why, consider the diagram in Fig. 1.4(d), which represents one of the terms in $\Omega_2^{\mathrm{C}}$. Within a second-order ladder approximation to $\Delta_3$, diagram 1.4(b) is included within

1.4(d). Thus three- and higher-body effects are incorporated into the cumulants $\Delta_3$ and $\Delta_4$ by the CSEs or ICSEs, even when these effects are absent from approximate reconstruction functionals. In effect, solution of these equations corresponds to a partial summation of the perturbation series for $D_2$, in the case of CSE(2), or $\Delta_1$ and $\Delta_2$, in the case that ICSE(1) and ICSE(2) are solved simultaneously. The connection between reconstruction and solution of coupled Green's function equations of motion, which are time-dependent hierarchies analogous to the CSE($p$) hierarchy, has received some attention,[70,71] though a more thorough exploration of this connection would be welcome.

## REFERENCES

1. F. Colmenero and C. Valdemoro, Int. J. Quantum Chem. **51**, 369 (1994).
2. C. Valdemoro, Reduced density matrix versus wave function: Recent developments, in *Strategies and Applications in Quantum Chemistry*, edited by Y. Ellinger and M. Defranceschi, page 55, Kluwer, Dordrecht, 1996.
3. C. Valdemoro, L. M. Tel, and E. Pérez-Romero, Adv. Quantum Chem. **28**, 33 (1997).
4. C. Valdemoro, D. R. Alcoba, and L. M. Tel, Int. J. Quantum Chem. **93**, 212 (2003).
5. C. Valdemoro, L. M. Tel, and E. Pérez-Romero, Critical questions concerning iterative solution of the contracted Schrödinger equation, in *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski, Plenum, New York, 2000.
6. C. Valdemoro, L. M. Tel, E. Pérez-Romero, and A. Torre, J. Mol. Struct. (Theochem) **537**, 1 (2001); erratum: **574**, 255 (2001).
7. K. Yasuda and H. Nakatsuji, Phys. Rev. A **56**, 2648 (1997).
8. H. Nakatsuji and K. Yasuda, Phys. Rev. Lett. **76**, 1039 (1996).
9. M. Nakata, M. Ehara, K. Yasuda, and H. Nakatsuji, J. Chem. Phys. **112**, 8772 (2000).
10. M. Ehara, M. Nakata, H. Kou, K. Yasuda, and H. Nakatsuji, Chem. Phys. Lett. **305**, 483 (1999).
11. K. Yasuda, Phys. Rev. A **59**, 4133 (1999).
12. H. Nakatsuji, Density equation theory in chemical physics, in *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski, page 85, Plenum, New York, 2000.

13. D. A. Mazziotti, Int. J. Quantum Chem. **70**, 557 (1998).

14. D. A. Mazziotti, J. Chem. Phys. **116**, 1239 (2002).

15. D. A. Mazziotti, Phys. Rev. A **60**, 3618 (1999).

16. D. A. Mazziotti, Phys. Rev. A **57**, 4219 (1998).

17. L. Cohen and C. Frishberg, Phys. Rev. A **13**, 927 (1976).

18. H. Nakatsuji, Phys. Rev. A **14**, 41 (1976).

19. H. Nakatsuji, Theor. Chem. Acc. **102**, 97 (1999).

20. A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).

21. H. Kummer, J. Math. Phys. **8**, 2063 (1967).

22. R. M. Erdahl, Int. J. Quantum Chem. **13**, 697 (1978).

23. E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic, New York, 1976.

24. A. J. Coleman and V. I. Yukalov, *Reduced Density Matrices: Coulson's Challenge*, Springer, Berlin, 2000.

25. F. Colmenero, C. Pérez del Valle, and C. Valdemoro, Phys. Rev. A **47**, 971 (1993).

26. F. Colmenero and C. Valdemoro, Phys. Rev. A **47**, 979 (1993).

27. D. A. Mazziotti, Chem. Phys. Lett. **326**, 212 (2000).

28. W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **110**, 2800 (1999).

29. W. Kutzelnigg and D. Mukherjee, Chem. Phys. Lett. **317**, 567 (2000).

30. D. Mukherjee and W. Kutzelnigg, J. Chem. Phys. **114**, 2047 (2001); erratum: **114**, 8226 (2001).

31. W. Kutzelnigg and D. Mukherjee, J. Chem. Phys. **116**, 4787 (2002).

32. W. Kutzelnigg, Int. J. Quantum Chem. **95**, 404 (2003).

33. D. A. Mazziotti, Chem. Phys. Lett. **289**, 419 (1998).

34. D. A. Mazziotti, Cumulants and the contracted Schrödinger equation, in *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski, page 139, Plenum, New York, 2000.

35. P. Ziesche, Cumulant expansions of reduced densities, reduced density matrices, and Green's functions, in *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski, page 33, Plenum, New York, 2000.

36. P. Ziesche and F. Tasnádi, Int. J. Quantum Chem. **100**, 495 (2004).
37. L. Lain, A. Torre, and R. Bochicchio, J. Chem. Phys. **117**, 5497 (2002).
38. J. E. Harriman, Phys. Rev. A **65**, 052507 (2002).
39. R. Kubo, J. Phys. Soc. (Japan) **17**, 1100 (1962).
40. R. J. Bartlett and G. D. Purvis, Int. J. Quantum Chem. **14**, 561 (1978).
41. R. J. Bartlett and G. D. Pervis III, Phys. Scr. **21**, 255 (1980).
42. R. J. Bartlett, Coupled-cluster theory: An overview of recent developments, in *Modern Electronic Structure Theory, Part II*, edited by D. R. Yarkony, page 1047, World Scientific, Rivers Edge, NJ, 1995.
43. J. M. Herbert and J. E. Harriman, J. Chem. Phys. **117**, 7464 (2002).
44. M. Nooijen, M. Wladyslawski, and A. Hazra, J. Chem. Phys. **118**, 4832 (2003).
45. P.-O. Löwdin, Phys. Rev. **97**, 1490 (1955).
46. J. M. Herbert, *Reconstructive approaches to one- and two-electron density matrix theory*, PhD thesis, University of Wisconsin, Madison, WI (2003).
47. J. M. Herbert and J. E. Harriman, Phys. Rev. A **65**, 022511 (2002).
48. J. E. Harriman, Phys. Rev. A **19**, 1893 (1979).
49. K. Yasuda, Phys. Rev. A **65**, 052121 (2002).
50. W. Kutzelnigg, J. Chem. Phys. **77**, 3081 (1982).
51. W. Kutzelnigg and S. Koch, J. Chem. Phys. **79**, 4315 (1983).
52. W. Kutzelnigg, Quantum chemistry in Fock space, in *Aspects of Many-Body Effects in Molecules and Extended Systems*, edited by D. Mukherjee, volume 50 of *Lecture Notes in Chemistry*, page 35, Springer-Verlag, Berlin, 1989.
53. T. Arai, J. Chem. Phys. **33**, 95 (1960).
54. P. E. Maslen, C. Oshsenfeld, C. A. White, and M. Head-Gordon, J. Phys. Chem. A **102**, 2215 (1998).
55. P. Ziesche, Solid State Commun. **82**, 597 (1992).
56. A. J. Coleman and I. Absar, Int. J. Quantum Chem. **18**, 1279 (1980).
57. E. H. Lieb, Phys. Rev. Lett. **46**, 457 (1981); erratum: **47**, 69 (1981).
58. M. Levy, Correlation energy functionals of one-matrices and Hartree-Fock densities, in *Density Matrices and Density Functionals*, edited by R. Erdahl and V. H. Smith, Jr., page 479, Reidel, Dordrecht, Netherlands, 1987.

59. C. de Dominicis and P. C. Martin, J. Math. Phys. **5**, 14 (1964); *ibid*. **5**, 31 (1964).

60. S. Weinberg, Phys. Rev. **133**, B232 (1964).

61. S. Weinberg, *The Quantum Theory of Fields, Vol. I: Foundations*, Cambridge University Press, 1995.

62. F. Harris, Int. J. Quantum Chem. **90**, 105 (2002).

63. R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem*, McGraw-Hill, New York, 2nd edition, 1976.

64. F. E. Harris, H. J. Monkhorst, and D. L. Freeman, *Algebraic and Diagrammatic Methods in Many-Fermion Theory*, Oxford University Press, New York, 1992.

65. M. Nooijen, J. Chem. Phys. **111**, 8356 (1999).

66. D. A. Mazziotti and R. M. Erdahl, Phys. Rev. A **63**, 042113 (2001).

67. C. Garrod and J. Percus, J. Math. Phys. **5**, 1756 (1964).

68. P. Piecuch and K. Kowalski, In search of the relationship between multiple solutions characterizing coupled-cluster theories, in *Computational Chemistry: Reviews of Current Trends*, edited by J. Leszczynski, volume 5, page 1, World Scientific, New York, 2000.

69. J. M. Herbert, Phys. Rev. A **66**, 052502 (2002).

70. R. D. Mattuck and A. Theumann, Adv. Phys. **20**, 721 (1971).

71. S.-J. Wang, W. Zuo, and W. Cassing, Nucl. Phys. A **573**, 245 (1994).