Diagrammatic quantum field formalism for localized electrons

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We introduce a diagrammatic quantum field formalism for the evaluation of normalized expectation values of operators, and suitable for systems with localized electrons. It is used to develop a convergent series expansion for the energy in powers of overlap integrals of single-particle orbitals. This method gives intuitive and practical rules for writing down the expansion to arbitrary order of overlap, and can be applied to any spin configuration and to any dimension. Its applicability for systems with well localized electrons has been illustrated with examples, including the two-dimensional Wigner crystal and spin-singlets in the low-density electron gas.

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I. INTRODUCTION

In the last two decades considerable effort in the theory of electronic structure has been focused on the development of methods where the time for computing ground state properties scales linearly with the size of the system, referred to as $O(N)$ methods, $N$ being the number of electrons in the system. A standard approach there is to make use of localized one-particle electron orbitals, and to circumvent their orthogonalization though various strategies and approximations in the subsequent energy minimization. Indeed, orthogonalization involves computationally intense algorithms; it is particularly impractical for geometrical optimizations, and it is actually intractable when the $N$-body electron wave function is to be written as a linear combination of Slater determinants made from different single-particle orbitals (i.e. for a general spin state).

The use of non-orthogonal orbitals, on the other hand, poses its own difficulties, because the antisymmetrization of the many-body wave function in this case introduces terms of a convergent series expansion of overlap integrals of single-particle orbitals. The Hamiltonian of this system is given in atomic units by

$$\hat{H} = \sum_{j=1}^{N_e} \frac{\hat{p}_j^2}{2} + \sum_{j=1}^{N_i} \frac{\hat{p}_j^2}{2M_j} + \frac{1}{2} \int dr \int dr' \frac{1}{|r-r'|} \times \left[ \hat{\rho}^{(2)}(r,r') + \hat{\rho}^{(2)}(r,r') - 2\hat{\rho}^{(1)}(r)\hat{\rho}^{(1)}(r') \right],$$

where the indices $e$ and $i$ refer to electrons and ions, respectively, $\hat{p}_j$ is the momentum operator of electron $j$, $\hat{P}_j$ and $M_j$ are the momentum operator and the mass of ion $j$, and $\hat{\rho}^{(1)}$ and $\hat{\rho}^{(2)}$ are the one- and two-particle density operators defined respectively by

$$\hat{\rho}^{(1)}(r) = \sum_j \delta(r - r_j),$$

and

$$\hat{\rho}^{(2)}(r,r') = \hat{\rho}^{(1)}(r)\hat{\rho}^{(1)}(r') - \delta(r - r')\hat{\rho}^{(1)}(r').$$

A standard approach to solving the eigenvalue problem for this system is, as a first step, to find the solutions of the electronic problem in the clamped nuclei approximation, where the ionic momenta are set to zero and their coordinates frozen. The Hamiltonian for this problem is
from (1),
\[ H = \sum_{j=1}^{N} \frac{\hat{p}_j^2}{2} + \frac{1}{2} \int dr \int dr' \frac{1}{|r - r'|} \]
\[ \times \left[ \hat{\rho}^{(2)}(r, r') - 2\hat{\rho}^{(1)}(r)\rho_b(r') \right] + U_b, \tag{4} \]
where \( \rho_b(r) \) is the classical density of the positive charge (ionic or that of a uniform rigid background), \( U_b \) is its self-energy, and we have simplified the notation by dropping the subscript \( e \) from quantities referring to the electrons.

In what follows we discuss the evaluation of the ground state properties of a system described by the Hamiltonian (1), and more specifically, the quantity
\[ E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \tag{5} \]

with \( |\Psi\rangle \) an \( N \)-electron trial state constructed from localized single-particle spatial orbitals centered at positions \( \{ \mathbf{R}_n \} \). Though (1) and (2) are formally independent of spin, we nevertheless also allow for an arbitrary spin configuration (i.e. correlation and even order) which can be specified by an appropriate set of spin orbitals.

Localized orbitals here mean that they diminish rapidly away from the localization centers \( \{ \mathbf{R}_n \} \). The limit where space can be divided into regions each occupied only by a single one-particle function corresponds to the semi-classical limit where the spin configuration becomes irrelevant and \( |\Psi\rangle \) is a product of single-particle states. When this is not the case, antisymmetrization of the many-body wave function and the resulting exchange effects become an important issue in determining the structural phase of the ground state.

Moving away from the semi-classical limit, and when the space orbitals are not orthogonal, requires a necessity to introduce terms in both the numerator and denominator of (2) that go as \( \sim O(S^{2n}N^n) \), where \( S \) is an overlap integral between one-electron wave functions, and \( n = 0, 2, 3, \ldots \). The resulting series are obviously divergent as \( N \to \infty \) irrespective of how small but finite \( S \) is. Here, we will deal with these problems by viewing the overlap effects as a formal “quantum perturbation,” which introduces some scattering of the single-particle amplitudes. The normalization of (2) is then achieved in a diagrammatic approach without an explicit inversion of an overlap matrix or a requirement to introduce a cut-off radius for the localized functions. The topology of the connected diagrams that give a convergent and finite expansion for the energy (per electron) will be determined by the set \( \{ \mathbf{R}_n \} \).

The remainder of the paper is organized as follows: In Section III we summarize a quantum field theoretical notation, used previously by van Dijk and Vertege\footnote{A. van Dijk and Y. Vertege, “Quantum field theory and applications in solid state physics.”} and later by Moutopoulos and Ashcroft\footnote{A. Moutopoulos and N. Ashcroft, “Quantum field theory and applications in solid state physics.”} for describing Wigner crystals. All matrix elements relevant for computing the energy are constructed from products of field operators. Their anticommutation relations are then used in Section IV to develop a diagrammatic language for evaluating the matrix elements. In Section V we show that the taking of a ratio of matrix elements leads to a linked cluster expansion. First, an algebraic expansion is obtained by generalizing a mathematical device used by Abarenkov\footnote{D. Abarenkov, “Quantum field theory and applications in solid state physics.”} in the context of a valence-bond method. Next, the new formalism is used to prove rigorously that the expansion is convergent and is topologically equivalent to linked clusters of closed-loop diagrams. A recipe and an example for calculating the energy are presented in Section VI. Further applications and uses of the method are discussed in Section VII.

II. QUANTUM FIELD THEORETICAL NOTATION

In the formalism of second quantization (requiring specification of an initial set of single-particle states), the kinetic energy and the density operators in (1) can be written in the forms (atomic units are used throughout):
\[ \hat{T} = \sum_{k, s} \frac{k^2}{2} c_{k, s}^\dagger c_{k, s}, \tag{6} \]
\[ \hat{\rho}^{(1)}(r) = \sum_{s} \psi_s(r) \psi_s^\dagger(r), \tag{7} \]
and
\[ \hat{\rho}^{(2)}(r, r') = \sum_{s, s'} \psi_{s'}(r') \psi_{s'}^\dagger(r') \psi_s(r) \psi_s^\dagger(r), \tag{8} \]
where \( c_{k, s}^\dagger \) and \( c_{k, s} \) are respectively creation and annihilation operators for an electron in a plane wave state with a wave vector \( k \) and spin \( s \), and \( \psi_s^\dagger(r) \) and \( \psi_s(r) \) are the usual field operators, i.e.
\[ \psi_s(r) = \frac{1}{\sqrt{V}} \sum_k c_{k, s}^\dagger(r) e^{i k \cdot r}, \tag{9} \]
which create and annihilate a Fermion with spin \( s \) at position \( r \). A general state of the system assumes the form
\[ |\Psi\rangle = \sum_{s_1, \ldots, s_N} \int dr_1 \cdots dr_N F(r_1, s_1; \ldots; r_N, s_N) \times \psi_{s_1}^\dagger(r_1) \cdots \psi_{s_N}^\dagger(r_N) |0\rangle. \tag{10} \]
Here \( |0\rangle \) denotes the vacuum state, and the antisymmetrization of the wave function is implicitly built into (10) through the anticommutation relations of the field operators, namely
\[ \{ \psi_s(r), \psi_{s'}^\dagger(r') \} = \delta_{s, s'} \delta(r - r'), \tag{11} \]
and
\[ \{ \psi_s(r), \psi_{s'}(r') \} = \{ \psi_s^\dagger(r), \psi_{s'}^\dagger(r') \} = 0. \tag{12} \]
In variational terms the problem is to determine the amplitude function $F$ which minimizes $\langle \mathbf{r} \rangle$. Because we want to construct the wavefunction from $N$ single-particle space orbitals, the choices for $F$ are linear combinations of products of single particle functions, each product representing a particular fixed-spin configuration (the standard Hartree-Fock approximation). For example, the simplest ansatz, corresponding to a ferromagnetic (FM) state is

$$F(\mathbf{r}_1, s_1; \ldots; \mathbf{r}_N, s_N) = \prod_{i=1}^{N} f_i (\mathbf{r}_i - \mathbf{R}_i),$$

where $f_i (\mathbf{r}_i - \mathbf{R}_i)$ indicates the (normalized for convenience) wavefunction of an electron localized at some position $\mathbf{R}_i$.

Next, following van Dijk and Vertogen, we introduce the operators $d_i^\dagger$ and $d_i$, defined by

$$d_i^\dagger = \int d\mathbf{r} \psi_i^\dagger (\mathbf{r}) f_i (\mathbf{r} - \mathbf{R}_i),$$

which create and annihilate an electron localized at position $\mathbf{R}_i$, with a one-particle function $f_i (\mathbf{r})$, and with spin $s_i$. A state corresponding to a particular fixed-spin configuration, can now be written as

$$|\Phi\rangle = \left( \prod_{i=1}^{N} d_i^\dagger \right) |0\rangle,$$

and if we label all such states by, say $p$, a general state of the system can be written as a linear combination of terms of the form $|\Phi_p\rangle$, i.e.

$$|\Psi\rangle = \sum_p C_p |\Phi_p\rangle.$$  

For example, a state corresponding to spin-singlet pairs of electrons will be described by

$$|\Psi\rangle = \prod_{i=1}^{N/2} \left( d_i^\dagger d_{i+1}^\dagger - d_{i+1} d_i \right) |0\rangle.$$  

Here the up and down arrows explicitly indicate the spin to be associated with the given operator, and it is clear that the electrons do not have definite spins but are nevertheless grouped in pairs where the two electrons of each pair always have antiparallel spins.

From (11), (12), and (13), it is straightforward to derive the following anticommutation relations for the newly defined creation and annihilation operators, namely:

$$\{d_i, d_j^\dagger\} = \delta_{s_i, s_j} S(ij), \quad (18)$$

and

$$\{d_i, d_j\} = \{d_i^\dagger, d_j^\dagger\} = 0.$$  

where $S(ij)$, a key quantity in what follows, is

$$S(ij) = \int d\mathbf{r} f_i^*(\mathbf{r} - \mathbf{R}_i) f_j (\mathbf{r} - \mathbf{R}_j), \quad (20)$$

the overlap integral of two single-particle wavefunctions centered at $\mathbf{R}_i$ and $\mathbf{R}_j$. In addition,

$$\{\psi_s (\mathbf{r}), d_i^\dagger\} = \delta_{s, s_i} f_i (\mathbf{r} - \mathbf{R}_i), \quad (21)$$

and

$$\{\psi_s (\mathbf{r}), d_i\} = \{\psi_s^\dagger (\mathbf{r}), d_i^\dagger\} = 0.$$  

Further, if $f_i (\mathbf{k})$ is the Fourier transform of $f_i (\mathbf{r})$, then for a system of dimensionality $D$,

$$\{c_{k, s}, d_i\} = \{c_{k, s}^\dagger, d_i^\dagger\} = 0.$$  

### III. DIAGRAMMATIC EVALUATION OF MATRIX ELEMENTS

Within the formalism of the previous section, all matrix elements of interest for the computation of the the energy assume the general form

$$\langle 0 | ABC \cdots Y Z | 0 \rangle,$$

where $A, B, C, \ldots$, etc. are creation and annihilation operators whose anticommutation relations in terms of localized single-particle functions have just been established. We now proceed to interpret these quantities as a sum of closed loop diagrams in a language very similar to that of standard field-theoretical and many-body methods.

We start by selecting an arbitrary labeling order of all distinct operators of interest; this can be done without loss of generality. Distinctions will be based on the label $i$ for the $d_i$, $\mathbf{r}$ for the $\psi_s (\mathbf{r})$, and $\mathbf{k}$ for the $c_{k, s}$ operators; the spin label will be irrelevant. Next, we define a $T$-product of operators, $T(ABC \cdots)$, which is a product of the operators $A, B, C, \ldots$, but written in such an order that all annihilation operators are on the left and in descending order of their labels, all creation operators are on the right of the annihilation operators and in ascending order of their labels, all creation operators are on the right of the annihilation operators and in ascending order of their labels, and the product is multiplied by $(-1)^P$, where $P$ is the number of permutations needed to obtain the $T$ product from $ABC \cdots$. For example,

$$T(d_2 d_3 d_1^\dagger d_4^\dagger d_i) = (-1)^3 d_3 d_2 d_1^\dagger d_i^\dagger.$$  

Next, we define an $N$-product (normal product) of operators, $N(ABC \cdots)$, which is a product of the operators $A, B, C, \ldots$, where all creation operators are on the left...
of all annihilation operators, and the product is multiplied by \((-1)^P\), with \(P\) being the number of permutations needed to obtain the \(N\)-ordering from \(ABC \cdots\). For example,

\[
N(d_1d_2d_3) = (−1)^2d_3^\dagger d_1d_2 = (−1)^3d_3^\dagger d_2d_1.
\]  

(27)

We can now define a pairing, or a contraction of two operators as

\[
A^cB^e = T(AB) - N(AB)
\]

\[
= \begin{cases} 
\{A, B\}, & \text{if } AB \text{ is } T\text{-ordered} \\
-\{A, B\}, & \text{if } AB \text{ is not } T\text{-ordered}
\end{cases}
\]

(28)

and then we have the equivalent of Wick’s theorem for our problem. This states that a \(T\)-product can be expressed as a sum of all possible \(N\)-products with all possible contractions, i.e.,

\[
T(ABC \cdots YZ) = N(ABC \cdots YZ) + N(A^cB^eC \cdots YZ) + \cdots + N(A^cB^eC^a \cdots Y^bZ^c).
\]

(29)

The validity of the above relation can be verified by inspection, but it is also not difficult to prove by induction.

Next, taking the vacuum expectation values of (28) and (29), and using the fact that by the definition of an \(N\)-product its vacuum average is zero when the product contains any uncontracted operators, we have

\[
A^cB^e = \langle 0|T(AB)|0 \rangle,
\]

(30)

and

\[
\langle 0|T(ABCD \cdots YZ)|0 \rangle = \langle 0|T(AB)|0 \rangle \langle 0|T(CD)|0 \rangle \cdots \langle 0|T(YZ)|0 \rangle ± \langle 0|T(AC)|0 \rangle \langle 0|T(BD)|0 \rangle \cdots \langle 0|T(YZ)|0 \rangle \pm \cdots
\]

(31)

where the \(\pm\) signs correspond to the parity of the permutation of the operators \(ABC \cdots XYZ\). As a consequence, any matrix element of the form (25) is evaluated in complete analogy with correlation functions in field theory.

Accordingly, we now develop a diagrammatic description for such matrix elements. The operators we are dealing with have three attributes: a label associated with the localization center of a one-particle function (for the \(d_i\) operators these functions are the \(f_i(r)\)’s, for the \(\psi_s(\mathbf{r})\) operators the \(\delta(r)\)’s, and for the \(c_{s,k}\) operators, the \(\bar{f}_i(k)\)’s,); a spin orientation; and every operator is either a creation or annihilation character. So, we will draw points to represent the set of labels of the operators (these points can obviously be re arranged to reflect the actual topology of the set \(\{\mathbf{R}_i\}\), and arrows pointing away from or towards them for creation or annihilation operators, respectively. In addition, we will indicate the spin with a bar across the arrows for spin up operators, resulting in what we will refer to as plus and minus arrows. For example,

\[
d_{i,\uparrow} = \overline{1_i}, \quad d_{i,\downarrow} = 1_i
\]

(32)

and similarly for the \(\psi_s(\mathbf{r})\) and \(c_{s,k}\) operators. To extend the analogy within the language of field theory even further, we will call the points associated with the \(d_i\) operators vertices, and those associated with the \(\psi_s(\mathbf{r})\) and \(c_{s,k}\) operators external points; the reason for this choice will become clear later.

In this construction, a pairing of two operators is represented by a line connecting the points associated with them, and having a direction determined by their ordering. When the operators are \(T\)-ordered, the lines will follow the arrows of the points they connect. Also, because the commutation relations of opposite spin operators are zero, only lines connecting either plus or minus arrows need be considered. If it is not possible to connect all points in this fashion, the corresponding matrix element is zero. This means that if all operators are present in the product as creation-annihilation pairs (each point has two arrows, one pointing at it and one away from it), the resulting non-zero diagrams are a collection of closed loops only.

It is now easy to see that after a couple of permutations the expectation values of the kinetic energy and density operators (32)-(35) can be brought to the form (31), where all operators are present in creation-annihilation pairs but all terms involving pairings between the \(\psi_s(\mathbf{r})\) and the \(c_{s,k}\) operators have canceled out. Therefore, all relevant matrix elements can indeed be evaluated as the sum of all possible closed-loop diagrams that can be constructed by connecting all vertices and external points according to the rules described above. The value of each diagram is then a product of the values of each line connecting two points, and the value of each such line is the anticommutation relation of the operators represented by the points. In addition, a sign must be associated with each diagram, which is given by

\[
(−1)^{n_e} \prod_l (−1)^{n_l−1}
\]

(34)

where \(n_e\) is the number of external points, the product is over all (closed) loops in the diagram and \(n_l\) is the number of lines (or points) in each loop; the one-point loop diagrams obviously have no influence on the sign. The formal proof of (34) is straightforward (e.g., by induction).

By way of example, and to illustrate the rules derived so far, we show the diagrammatic expansion of the one-particle density, \(\langle \Psi | \hat{n}_{1,\uparrow}(\mathbf{r}) | \Psi \rangle\), where \(| \Psi \rangle\) is an \(N\)-
electron ferromagnetic state; thus,
\[
\langle \Psi | \hat{\beta}^{(1)}(r) | \Psi \rangle = \delta(r) - \langle \Psi | \hat{\psi}(r) \hat{\psi}^\dagger(r) | \Psi \rangle
\]
\[
= \sum_{i \neq j} \int \frac{d^3r}{(2\pi)^3} \frac{1}{i} \left[ \frac{1}{\beta} \left( \frac{e^{\beta \phi(i,j,r)}}{\cosh \beta \phi(i,j,r)} - \cosh \beta \phi(i,j,r) \right) \right]
\]
\[
+ \sum_{i \neq j} \sum_{k \neq l} \int \frac{d^3r}{(2\pi)^3} \frac{1}{i} \left[ \frac{1}{\beta} \left( \frac{e^{\beta \phi(i,j,r)}}{\cosh \beta \phi(i,j,r)} - \cosh \beta \phi(i,j,r) \right) \right]
\]
\[
+ \cdots
\]
(35)

Here the filled points indicate summation over all vertices, and we have omitted one-point loops, which are equal to unity. In the semi-classical limit, or if the single-particle functions are orthogonal, only the first diagram above remains. The overlap-order of a diagram increases, and their values diminish exponentially with increasing size of the loops. The presence of disconnected loops is generally what causes such quantities to diverge in the thermodynamic limit. As with other many-body methods, this problem is removed by the normalization of the expectation values, which leads to the equivalent of a linked cluster expansion.

IV. CONSTRUCTION OF A LINKED CLUSTER EXPANSION

Let $|N\rangle$ be a product (or a linear combination of products) of $N$ creation field operators acting on the vacuum state. As we showed above, $(N|N)$ can be thought of as a sum of all possible closed-loop diagrams connecting some representative $N$ points. Then, we can write:
\[
(N|N) = \sum_{n_1, \ldots, n_N} C(n_1, \ldots, n_N),
\]
(36)
where $C(n_1, \ldots, n_N)$ is the class of all diagrams containing exactly $n_1$ 1-point loops, $n_2$ 2-point loops, and so on.

Next, let us define a generating function,
\[
Q_N(t) = \sum_{n_1, \ldots, n_N} C(n_1, \ldots, n_N) t^{N-n_1},
\]
(37)
of a standard continuous variable, $t$, and because $\sum_k n_k = N$, it is clear that
\[
Q_N(0) = C(N, 0, \ldots, 0),
\]
(38)
\[
Q_N'(0) = 0,
\]
(39)
\[
Q_N''(0) = 2! C(N - 2, 1, 0, \ldots, 0),
\]
(40)
\[
Q_N'''(0) = 3! C(N - 3, 0, 1, \ldots, 0),
\]
(41)
etc., or more generally, for the $m$th derivative of $Q_N(t)$:
\[
Q_N^{(m)}(0) = m! \sum_{n_2, \ldots, n_N} C(N - m, n_2, \ldots, n_N),
\]
(42)
subject to the constraint $\sum_k n_k = m$.

Furthermore, we can also define a function, associated with $Q_N(t)$, by
\[
R_n(t) = \frac{Q_{N+n}(t)}{Q_N(t)}
\]
(43)
and think of the original $N$ points as vertices representing one-particle functions, and the additional $n$ points as external and representing an $n$-body operator $\hat{O}^{(n)}$. Then, within this construction,
\[
\frac{\langle \Psi | \hat{O}^{(n)} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = R_n(1) - \left\{ \text{diagrams with lines connecting external points} \right\}
\]
(44)
and a diagrammatic expansion of the above can be obtained by considering the Taylor expansion of $R(t)$ around $t = 0$, namely,
\[
R_n(1) = \sum_{m=0}^{\infty} \sum_{i=0}^{m} \frac{1}{i!} Q_N^{(i)}(0) \frac{1}{(m-i)!} \left( \frac{1}{Q_{N+n}(0)} \right)^{(m-i)}. \]
(45)

For our further discussion it will be convenient to denote by $V_i$ the value of all diagrams that can be constructed out of any $i$ vertices, and that do not contain 1-point loops. Similarly, $X_i$ will indicate all such diagrams, but where the $i$ points may include external points. Clearly,
\[
V_i = \frac{1}{i!} Q_N^{(i)}(0),
\]
(46)
and
\[
X_i = \frac{1}{i!} Q_{N+n}(0).
\]
(47)

A. Fixed-spin configuration

First, we consider the case when $|N\rangle$ is a single product of $d_i^\dagger$ operators. In such a fixed-spin configuration, $Q_N(0) = 1$, and $\frac{1}{(m-i)!} \left( \frac{1}{Q_{N+n}(0)} \right)^{(m-i)}$ can be decomposed simply as
\[
\frac{1}{(m-i)!} \left( \frac{1}{Q_{N+n}(0)} \right)^{(m-i)} = W_{m-i}
\]
(48)
\[
= \sum_j X_{j_1} \cdots X_{j_{m-i}},
\]
where \( j_1 + \cdots + j_{m-i} = m - i \). Then, because \( R_0(1) = 1 \), we have \( \sum_{i=0}^{m} X_i W_{m-i} = 0 \), and it follows that:

\[
R_n(1) = \sum_{m=0}^{\infty} \sum_{i=0}^{m} (V_i - X_i) W_{m-i} = 1 + (V_2 - X_2) + (V_3 - X_3) + |V_4 - X_4 - 6X_2(V_2 - X_2)| + \cdots
\]  

(49)

This expression now represents a convergent linked cluster expansion. It is easy to see that the second and third terms above are simply two-point and three-point loops involving the external points. The higher order terms are more complicated, but they are equivalent to chained loops connected to the external points. For example, the fourth term is a sum of all four-point loops involving external points and a product of two two-point loops, either chained or not, but connected to two different external points. To prove that (49) is indeed convergent and to illustrate the diagrammatic rules, we present a second construction for the linked cluster expansion.

Thus, we will now consider only the case when \( n = 1 \) and introduce the following notation: \( L_{r_{i_1} \cdots i_m} \) will denote a single loop connecting all points labeled \( r, i_1, \ldots, i_m \), \( |N - \{i_1, \ldots, i_m\}| \) will be a state obtained by removing operators \( d_{i_1}^\dagger \cdots d_{i_m}^\dagger \) from \( |N, n \rangle \), and \( \bar{R}_{i_1 \cdots i_m} \) will then be defined by the ratio

\[
\bar{R}_{i_1 \cdots i_m} = \frac{\langle N - \{i_1, \ldots, i_m\}|N - \{i_1, \ldots, i_m\} \rangle}{\langle N|N \rangle},
\]  

(50)

and \( D_{i_1 \cdots i_m} \) will denote the subset of all diagrams from \( \langle N|N \rangle \), which have at least one non-unity loop connected to any of the points \( \{i_1, \ldots, i_m\} \), divided by \( \langle N|N \rangle \). Then, \( R_1(1) \) can be expanded in the following way:

\[
R_1(1) = L_r + \frac{1}{m!} \sum_{m=1}^{N} L_{r_{i_1} \cdots i_m} \bar{R}_{i_1 \cdots i_m},
\]  

(51)

where summation over repeated indexes is implied, and \( 1/m! \) is to take account of repetitions.

To every \( \bar{R}_{i_1 \cdots i_m} \) term, we now add and subtract \( D_{i_1 \cdots i_m} \) leading to

\[
R_1(1) = L_r + \frac{1}{m!} \sum_{m=1}^{N} L_{r_{i_1} \cdots i_m} \bar{R}_{i_1 \cdots i_m} - \frac{1}{m!} \sum_{m=1}^{N} L_{r_{i_1} \cdots i_m} D_{i_1 \cdots i_m}.
\]  

(52)

Subsequently, the terms \( D_{i_1 \cdots i_m} \) can be decomposed into products of loops connected to the points \( \{i_1, \ldots, i_m\} \) and ratios \( \bar{R}_{i_1 \cdots i_m} \). By repeating this procedure, we are building a chained structure of loops connected to the external point, \( r \). Every repetition contributes a minus sign and exactly one more (surviving) loop to the chain. To see the latter, consider a particular element, say

\[
D_{12} = L_{12} R_{12} + 2 \sum_{m=1}^{N-1} L_{1j_1 \cdots j_m} R_{12j_1 \cdots j_m} + \sum_{m,n=1}^{N-2} L_{1j_1 \cdots j_m} L_{2i_1 \cdots i_n} R_{12j_1 \cdots j_m i_1 \cdots i_n}.
\]  

(53)

The first two terms above add one, while the third adds two loops to the cluster at \( i_1 \) and \( i_2 \). However, if the recursion procedure is applied to the second term once again, it will lead to two sums equal to the third term in (53), but with opposite sign. Thus, each step of the expansion contributes exactly one loop to the linked cluster that survives subsequent iterations, a minus sign to the diagram, and importantly, increases its order by \( S^2 \).

The expansion operation, (52), can be applied to all members of \( \bar{R}_{i_1 \cdots i_m} \) any number of times, \( M \), for any given \( N \), until we obtain a sum of all possible loops involving the external point, \( r \), chained to them \( 0, 1, 2, 3, \ldots \) connected loops (with repetitions) involving the \( N \) vertices, and a remaining leading term of the order

\[
O(S^2(N+M)) \frac{1}{\langle N|N \rangle^{N+M-\infty}}.
\]  

(54)

The construction can be generalized to the case with \( n_e \) external points by noting that there will be then simply \( n_e \) such linked clusters connected to the external points, or alternatively it can be seen by considering that \( R_n(1) = R_n^0(1) \), e.g.

\[
\frac{\langle N + |N + 2 \rangle}{\langle N|N \rangle} = \frac{\langle N + 2|N + 2 \rangle}{\langle N + 1|N + 1 \rangle} \cdot \frac{\langle N + 1|N + 1 \rangle}{\langle N|N \rangle}.
\]  

(55)

Summarizing to this point, the normalized expectation value of an \( n \)-body operator equals the sum of all diagrams where \( n = n_e \) external points are connected by a single loop to linked clusters of loops connecting vertices. Loops with lines connecting external points directly are not permitted, while any powers of vertex-only loops are allowed. We already saw that an \( n_e \)-point loop picks up a sign \(( -1)^{n_e} - 1 \). In addition, the construction of the linked-cluster expansion shows that the addition of every new loop alternates the sign, so a diagram with \( l \) loops, of which \( l_e \) connect external points, and \( n_e \) external points has to be multiplied also by \(( -1)^{n_e} \cdot (-1)^{l-l_e} \).

Altogether the result is that a diagram with a total of \( N_l \) lines connecting distinct points has a sign given by

\[
(-1)^{N_l + n_e - l_e}.
\]  

(56)

Continuing with the example of the one-particle density in a single-determinant many-body state, the normalization can be calculated using (56) and (54) on the more general result (52) and the expression (41) for the two-body operator.

\[
\frac{\langle N + 2|N + 2 \rangle}{\langle N + 1|N + 1 \rangle} \cdot \frac{\langle N + 1|N + 1 \rangle}{\langle N|N \rangle}.
\]  

(55)
Here, as before, filled dots indicate summation over all vertices, different labels mark distinct points, and the label $l(j)$ in the last two diagrams implies that the corresponding point may coincide with the point $j$. This series is an expansion of the density

$$\rho^{(1)}(r) = \rho_0(r) + \rho_1(r) + \rho_2(r) + \cdots,$$

(58)

where

$$\int dr \rho_0(r) = N,$$

(59)

and for $i \geq 1$

$$\int dr \rho_i(r) = 0.$$

(60)

Further, \( \rho_0(r) = \sum_i |f_i(r - R_i)|^2 \) is the density in the semi-classical limit, or if the one-particle functions were orthogonal; \( \rho_1(r) \equiv 0 \); and \( \rho_2(r), \rho_3(r), \rho_4(r), \ldots \) are the terms in curly brackets in (57), every one of which represents a different order of overlap. It is easy to see that they indeed satisfy (60), because

$$\int dr \int |i\rangle \rho_j^{(1)}(r) \langle j| = S(1) = i \quad \circ \quad j.$$

(61)

Each of the diagrams in the curly brackets in (57) represents a localized effective exchange charge and they can be grouped in pairs forming electric dipoles. The terms \( \rho_l(r) \), for \( i \geq 1 \), actually include summation over all vertices, and therefore represent higher order multipoles, e.g. \( \rho_2(r) \) is a quadrupole.

If we now return to the expansion in (45) and compare it with (57), we see that \( \rho_0(r) \) is given by \( X_2 - V_2 \). However, the term \( X_3 - V_3 \) gives only the single 3-point loop (with a minus sign) in \( \rho_2(r) \), so if (45) is truncated at this point, charge neutrality in the system will be violated. The required neutralizing part in \( \rho_2(r) \) comes from the next term in (45), which contains products of 2-point loops. With the diagrammatic formalism, on the other hand, it is intuitively straightforward to maintain charge neutrality by grouping all diagrams involving a given set of vertices.

As a second example, the diagrammatic expansion of the two-particle density, \( \rho^{(2)}(r,r') \), consists of the product \( \rho^{(1)}(r)\rho^{(1)}(r') \), which can be obtained from (57), and supplemented by another part with diagrams where a single loop is associated with both external points, \( r \) and \( r' \). Both parts contain overlap-dependent diagrams giving rise to exchange-correlation effects. Those coming from \( \rho^{(1)}(r)\rho^{(1)}(r') \) arise solely from the non-orthogonality of the one-particle functions; they are sometimes called indirect exchange terms and are usually responsible for the molecular bonding (not in a ferromagnetic, but spin-paired state, of course). The diagrams where both external points are linked with a single loop give rise to the so-called direct exchange, and some of them, for example

$$\begin{align*}
\text{(62)}
\end{align*}$$

survive even if the one-particle functions are orthogonal. Notice that direct exchange comes from parallel spin correlations, and indeed, we cannot form a loop such as (62) (even with more vertices) so long as any two electrons in it are in an antiferromagnetic arrangement. This is not the case for the indirect exchange, where \( r \) and \( r' \) are in separate loops. The qualitative differences between the direct and indirect exchange can also be seen from the fact that same-order overlap diagrams representing the two terms have opposite sign (see (60)). For instance, compare (62) with

$$\begin{align*}
\text{(63)}
\end{align*}$$

Thus, the diagrammatic language accurately captures the well known fact that the ground state electronic structure is often determined by the competition of the two types of exchange.

**B. General-spin configuration**

Dealing with a general-spin configuration means confronting the fact that \( |N \rangle \) must be a linear combination of state vectors, each one written as a product of \( N \) operators,

$$|N\rangle = \sum_{p=1}^{M} b_p |N\rangle_p,$$

(64)

here the \( b_p \)'s being arbitrary constants. Therefore, we have to consider \( M^2 \) different configurations resulting...
from \(\langle N|N\rangle\), each of them with \(N\) points but with different sets of arrows, representing creation and annihilation operators and their spins. The difficulties that now arise are related first, the fact that a given diagram can be present in more than one configuration, and second, to the consideration that not all diagrams can be constructed in all configurations. For example, the \(C(N,0,\ldots,0)\) class diagrams, which are simply (and only) one-point loops, exist only in the \(p(N|N)\) configurations, and there are \(M\) of them. Then,

\[
Q_N(0) = \sum_p b_p^2, \tag{65}
\]

rather than unity, so here we are obliged to keep a tally even of the one-point loops.

As a result of all this, formulating the expansion rules by following the linked-cluster construction outlined between Eqs. \(60\) and \(63\) might appear to become quite cumbersome for a general state because of the required book-keeping, even though there are no qualitative differences with the single-determinant case. However, because the ferromagnetic state leads to a complete set of diagrams for a given set of points \(\{\mathbf{R}_i\}\), we can reasonably expect that the linked-cluster expansion for a general state can be obtained from that of a ferromagnetic state (e.g. \(67\)) by multiplying every term in it by a coefficient related to the frequency of occurrence of its elements over all spin configurations resulting from \(\langle N|N\rangle\).

This conclusion can be verified by examining Eq. \(49\). It is still valid when \(\langle N\rangle\) is in the general form \(44\), however, the \(W_{m-i}\)'s, which were previously given by \(45\), now contain \(Q_{N+n}(0)\) for the power \(m - i + 1\) in the denominator, namely:

\[
W_{m-i} = \frac{1}{Q_{N+n}(0)} \sum_{j_1,\ldots,j_{m-i}} \frac{X_{j_1} \cdots X_{j_{m-i}}}{Q_{N+n}(0)}, \tag{66}
\]

where \(Q_{N+n}(0)\) is also given by \(65\). The meaning of the \(V_i\)'s and \(X_i\)'s also changes; while in Section \(\text{V.A}\) they were equal to the two-or-more-point loops that can be constructed out of \(i\) points, now we have to sum over all configurations coming from \(\langle N|N\rangle\) where these same loops can be formed and where the remaining \(N-i\) points form one-point loops (i.e. they represent a fixed spin state, \(\langle N - \{i\}|N - \{i\}\rangle\)). In practice, the latter condition actually greatly simplifies the calculations, as will be demonstrated in an example below. The final result therefore is that the expansion \(49\), and consequently the diagrammatic rules derived in Section \(\text{V.A}\) remain the same for the general case, but now every loop carries a coefficient, equal to

\[
\sum_{\{pp'\}} b_p b_{p'} \frac{1}{\sum_{p=1}^M b_p^2} \tag{67}
\]

where the sum over \(\{pp'\}\) is over all configurations \(p(N|N)_{p'}\) where (1) the given loop can be formed, and (2) all remaining points are of definite spins, i.e. either \(\big\langle\big\rangle\) or \(\big\rangle\). These coefficients can be thought of as weights of the various loops, and in the case when all the \(b_p\)'s are equal to unity, they are simply the fraction of all configurations in which the given loop diagram appears.

Continuing with the example of the one-particle density, the generalization of \(67\) is now:

\[
\rho^{(1)}(\mathbf{r}) = \left\{ \begin{array}{c}
\rho_{ijl} \left( \begin{array}{c}
\mathbf{r} \\
\mathbf{r}
\end{array} \right) + c_{ijl} \left( \begin{array}{c}
\mathbf{r} \\
\mathbf{r}
\end{array} \right)
\end{array} \right\}
\]

\[
+ c_{ij} c_{kl} \left( \begin{array}{c}
\mathbf{r} \\
\mathbf{r}
\end{array} \right) + \cdots \tag{68}
\]

Here, the coefficient associated with the two-point loop connecting \(\mathbf{r}\) and \(\mathbf{i}\) is unity for normalization reasons, and the terms in brackets must have the same coefficients in order to preserve the charge neutrality; both of these statements are actually easy to verify explicitly. So, to obtain the expansion to the given order of overlap for a particular spin state, it is only necessary to determine the coefficients for two- and three-point vertex loops, \(c_{ij}\) and \(c_{ijl}\) respectively. We will now show how this is done with the example of a spin-singlet paired state \(17\).

The wave-function in \(17\) is a linear combination of \(M = 2^{2N/2}\) products of field operators with \(b_p = \pm 1\), so \(\sum_p b_p^2 = 2^{N/2}\). If we pick a particular spin pair, it leads to four types of configurations in \(\langle \Psi|\Psi\rangle\):

(i) 
(ii) 
(iii) 
(iv) 

To determine \(c_{ij}\), we have to count all configurations where we can form a two-point loop out of \(i\) and \(j\), and form one-point loops of the remaining points. Thus, if \(i\) and \(j\) belong to the same pair, they must be either in state (iii) or (iv), thus bringing a factor of \(-2\). The remaining \(N-2\) points must be either in configuration (i) or (ii), of which there are \(2^{N/2}\), and all of them with positive sign. So, in this case, \(c_{ij} = -2^{1/2} 2^{N/2}/2^{N/2} = -1\). If \(i\) and \(j\) belong to different pairs, both of these points have to be either in (i) or (ii). This is because the remaining points from each pair must form one-point loops. From the remaining four combinations only two survive, because \(i\) and \(j\) must be associated with parallel spins, So,
the two pairs contribute two configurations, the remaining \(N - 2\) points, as before, give rise to \(\frac{1}{4}2^{N/2}\) possible diagrams with only one-point loops, and we therefore find \(c_{ij} = \frac{1}{2}\).

For \(c_{ijl}\), we have to consider 3-point loops; they can connect either 3 points all belonging to different pairs, or 3 points two of which can be from the same singlet pair. In the former case, all points must be in configurations (i) or (ii), as was the case with \(c_{ij}\), and then they all have to be associated with parallel spins. There are two such configurations, and the remaining \(N - 3\) points give \(\frac{1}{2}2^{N/2}\) more, so the result is that \(c_{ijl} = \frac{1}{2}\). If 2 of the 3 points belong to the same pair, they must be either in (iii) or (iv). Then, in either case, the remaining point must be in either (i) or (ii), but not in both. So, there are two options each carrying a minus sign. The remaining \(N - 2\) points give \(\frac{1}{4}2^{N/2}\) eligible combinations, and in this case \(c_{ijl} = -\frac{1}{2}\).

To summarize, we have determined that for the spin-singlet paired state \((17)\),

\[
c_{ij} = \begin{cases} 
-1, & \text{if } i \text{ and } j \text{ are in the same pair} \\
\frac{1}{2}, & \text{if } i \text{ and } j \text{ are not in the same pair,}
\end{cases}
\]

and \(c_{ijl} = \begin{cases} 
-\frac{1}{2}, & \text{if any 2 of } i, j, l \text{ are in the same pair} \\
\frac{1}{2}, & \text{if } i, j, l \text{ are from different pairs.}
\end{cases}\)

Result \((69)\) is in agreement with Refs. \(3\) and \(4\) but here it is obtained in a quite different way; and with \((70)\) we are going one step further, as we already have the next term in \((68)\) without further effort. In fact, the expansion \((68)\) has seven terms (if we open the brackets), however, with the diagrammatic language it is easy to see first, that only two of their coefficients are unique, and next to determine them.

\section{Energy Calculation}

In this section, we demonstrate the use of the diagrammatic technique for evaluating the energy of a system with localized electrons. First, we formulate general rules for such calculations, and then we apply them to a practical example.

\subsection{Diagrammatic rules}

To calculate the energy with the help of the diagrammatic language, we adhere to the following procedure:

1. Specify the localization points, \(\{\mathbf{R}_i\}\), for the single-particle functions, \(f_i(\mathbf{r})\), and decide the required order of overlap.

2. Determine the coefficients associated with the spin configuration for all diagrams up to the required order of overlap. The order of overlap of a diagram is usually equal to (but may be higher than) the number of interconnected vertices in it.

3. Form all connected, topologically non-equivalent and non-zero diagrams with one and two external points up to the required order of overlap following the rules described in Section IV.

4. Determine the signs and symmetry factors (multiplicity) of all diagrams.

5. Group diagrams involving the same vertices; each group represents either a direct or an indirect (with zero net charge) exchange term.

6. With each solid line associate an overlap integral:

\[
\mathbf{i} \quad \rightarrow \quad S(ij) = \int \! d\mathbf{r}_i (\mathbf{r} - \mathbf{R}_i) f_j(\mathbf{r} - \mathbf{R}_j),
\]

generally assumed to be small.

7. With each external \(k\)-point associate a kinetic energy term:

\[
\mathbf{i} \quad \rightarrow \quad T(ij) = \int \! d\mathbf{k} \frac{k^2}{2} f_i(\mathbf{k}) f_j(\mathbf{k}) e^{-i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}.
\]

8. With each pair of external points \(\mathbf{r}\) and \(\mathbf{r}'\) associate an interaction energy term:

\[
\mathbf{i} \quad \rightarrow \quad U(ij, kl) = \int \! dr \int \! dr' \frac{1}{|\mathbf{r} - \mathbf{r}'|} f_i(\mathbf{r}) f_j(\mathbf{r}) f_l(\mathbf{r}') f_m(\mathbf{r}'),
\]

where here \(f_i(\mathbf{r})\) stands for \(f_i(\mathbf{r} - \mathbf{R}_i)\), etc.

9. Sum over all vertex points, \(i, j, l, m\), and \(\mathbf{R}\).

The advantage in following this procedure is that all exchange-correlation terms originating from the non-orthogonality of the one-particle orbitals can be easily pre-summed, thus reducing the complexity of the problem to that of one with orthogonal orbitals. The computational cost is then limited by the efficiency for the evaluation of the Coulomb repulsion integrals \(U(ij, kl)\). Their computation can be carried out with existing algorithms that scale linearly beyond a given \(N\), for example, the linear scaling methods developed by Schwegler and Challacombe\(2\) for computation of the \(U(ij, kl)\) integrals based on multipole expansions.
B. Example: The two-dimensional Wigner crystal

As an illustrative example of the application of the procedure described above, we consider the case of the ground state of a 2-D Wigner crystal\(^2\) (WC) where the electrons are localized on a hexagonal lattice in the presence of a uniform, rigid and neutralizing background. For \(N\) electrons in an area \(A\), the background charge density is \(\rho_b = N/A = 1/\pi r_s^2\), which also defines the dimensionless density parameter \(r_s\). Quantum Monte Carlo calculations have predicted that the 2-D WC exists for \(r_s > 37.2\). The hexagonal lattice has primitive vectors

\[
a_1 = a(1, 0), \quad \text{and} \quad a_2 = \frac{a}{2}(1, \sqrt{3}),
\]

where \(a = \sqrt{\frac{a}{2} r_s}\) is the lattice parameter, and the electrons are localized on sites \(R_i = n_i a_1 + m_i a_2\).

With each electron, we associate a normalized Gaussian (trial) wavefunction in 2-D with width \(\sigma\), i.e.

\[
f(r - R_i) = \frac{1}{\sqrt{\pi \sigma^2}} e^{-((r-R_i)^2)/2\sigma^2}.
\]

The choice of Gaussians here is justified because the potential around the equilibrium positions of the electrons is close to harmonic. Finally, we will restrict our discussion to the antiferromagnetic (AFM) state - a spin-frustrated structure with alternating lines of up and down spins, e.g. an electron localized at \(R_i\) will have a positive (negative) spin if \(m_i\) is even (odd).

With these preliminaries, we can now proceed to calculate the energy per electron. The overlap integral between one-particle functions centered at \(R_i\) and \(R_j\) is

\[
S(ij) = e^{-R_{ij}^2/4 \sigma^2},
\]

where \(R_{ij} = R_i - R_j\). Typical values for \(\sigma\) can be estimated\(^2\) to be less than \(a/4\) and, therefore, the nearest neighbor (n.n.) overlap is \(S = S(a) \lesssim 1 \approx 0.37\). Since \(S^4 \approx 0.02\) and \(S^5 \approx 0.007\), inclusion of diagrams up to \(O(S^4)\) will guarantee a better than 1\% precision in the calculation of the total energy. The next n.n. (n.n.n.) distance in the triangular lattice is \(\sqrt{3}a\), which means that the n.n.n. overlap integral is \(S(\sqrt{3}a) = S^3\). Therefore, for the required precision we need to consider only n.n. overlaps because the two-vertex diagrams are of order \(S^2(\sqrt{3}a) = S^5\) and the three-vertex are of order \(S(a)S(\sqrt{3}a)S(a) = S^5\) when they involve n.n.n. overlaps.

The relevant coefficients associated with the spin configuration are

\[
c_{ij} = \delta_{s_i, s_j},
\]

and

\[
c_{ijl} = \delta_{s_i, s_l} \delta_{s_i, s_j} \delta_{s_j, s_l},
\]

where \(s_i\) indicates the spin of an electron localized at \(R_i\). For diagrams involving only n.n. overlaps, i.e. when \(R_{ij} = R_{jl} = a\), we have \(c_{ijl} = 0\), and we can also set:

\[
c_{ij} = \begin{cases} 1, & \text{if } R_{ij} = a_1 \\ 0, & \text{if } R_{ij} \neq a_1. \end{cases}
\]

Thus, the three-vertex \(O(S^3)\) diagrams vanish, and we are left with only two-vertex diagrams of order \(S^2\) and \(S^4\).

The relevant diagrams with one external point, together with their signs and multiplicity factors are:

\[
O(S^0): \quad \begin{array}{c} \includegraphics[width=0.3\textwidth]{diagram1.png} \end{array}
\]

\[
O(S^2): \quad \begin{array}{c} \includegraphics[width=0.3\textwidth]{diagram2.png} \end{array}
\]

\[
O(S^4): \quad \begin{array}{c} \includegraphics[width=0.3\textwidth]{diagram3.png} \end{array}
\]

Each of the \(O(S^2)\) diagrams above has in principle a symmetry factor of two – in the first diagram the external point can be connected to either \(i\) or \(j\), and in the second the three-point loop can go either clockwise or counterclockwise. However, this symmetry factor is taken care of when performing a sum over \(i\) and \(j\) and allowing repetition, e.g. \(\{i, j\} = \{1, 2; 2, 1\}\) (but \(i \neq j\). The \(O(S^4)\) diagrams have a multiplicity of three here, because in the triangular lattice there are three diagrams of each type, namely, in addition to those shown above, when \(l = i\), and with a \(i\)l loop instead of \(jl\) (for a different spatial or spin configurations we may have to write these explicitly).

Given\(^7\)-\(^9\), we associate the following kinetic energy terms:

\[
T(ii) + T(ii)S^2(ij) - T(ij)S(ij) + 3 \left[ T(ii)S^2(ij) - T(ij)S(ij) \right] S^2(jl),
\]

which with the choice of Gaussian wavefunctions have a simple analytical form, namely

\[
T(ij) = S(ij)T(0) \left(1 - \frac{R_{ij}^2}{4\sigma^2}\right).
\]

Here \(T(0) = 1/2\sigma^2\) is just the energy of a 2-D harmonic oscillator. Then, after summing over \(i\), \(j\), and \(l\), we obtain the kinetic energy per electron as:

\[
\frac{T}{N} = T(0) \left(1 + \frac{\alpha^2}{2\sigma^2} (S^2 + 3S^4)\right).
\]

The relevant diagrams with two external points, rep-
representing the electron-electron interaction energy are:

\[ O(S^0) = \frac{1}{2} \sum_{ij} \epsilon_{ij} \]

\[ O(S^2) = \sum_{ijkl} \epsilon_{ijkl} \]

\[ O(S^4) = 3 \sum_{ijkl} \epsilon_{ijkl} \]

After summing (82-84) over \( i,j,l \), and \( m \), the electron-electron interaction energy per electron is then given by:

\[ \frac{V_e}{N} = \frac{1}{2} \sum_{\mathbf{R} \neq 0} U(\mathbf{R}) \]

\[ + (2S^2 + 10S^4) \left( \sum_{\mathbf{R} \neq 0} U(\mathbf{R}) - U(\mathbf{R} + \mathbf{a}/2) \right) \]

\[ + S^2 \left[ 2U(\mathbf{a}/2) - U(0) \right] \]

\[ + 4S^4 \left[ 10U(\mathbf{a}/2) - 4U(\mathbf{a}) - 3U(0) \right], \]

where terms involving \( U(\mathbf{a}) \) and \( U(\mathbf{a}_1/2) \) have been added and subtracted in order to complete the second sum above, and \( U(0) = \sqrt{2\pi}/\sigma \) comes from the direct exchange. For the total interaction energy, the electron-background and background-background energies have to be added, which together with the first term in (87) can be evaluated by the Ewald lattice summation method. The second sum is equivalent to the interaction energy of an ionic lattice with opposite charges at \( \mathbf{R} \) and \( \mathbf{R} + \mathbf{a} \) and again is straightforward to obtain by the Ewald construction. Finally, the remaining terms require only the numerical computation of two integrals such as given by (88).

The solution thus obtained straightforwardly here, up to and including fourth order in overlap, is to be compared with Refs. [234], where similar problems are discussed but only up to \( O(S^2) \). The procedure can easily be extended, if needed, to higher orders.

VI. DISCUSSION AND FURTHER EXAMPLES

As with other diagrammatic techniques, the benefits here come from a translation of an algebraic formalism into a more intuitive diagrammatic language. It provides insight helpful for dealing with various spin correlations and overlap effects of arbitrary order. The diagrammatic rules also offer guidance for calculating normalized matrix elements in a most efficient way for a desired accuracy, while also preserving charge neutrality in the system. Violation of charge neutrality as a result of an approximate treatment of overlap effects may become a serious issue depending on the system size. We will illustrate this problem with an example of a system of spin singlets, which has been studied previously in the context of a low-density electron gas [234], but also has relevance for molecular systems.

Consider therefore a collection of \( n \) spin-singlet pairs of electrons (\( N = 2n \)). We will assume that the separations between pairs are sufficient so that interpair overlaps can be ignored. Without loss of generality we will also set all intrapair separations to be the same and equal to \( a \) (the relevant overlap integral being \( S = S(a) \)). For simplicity, we will examine only the exchange corrections to the kinetic energy; these can be easily determined to all
orders of intrapair overlap. With this construction, there are three types of diagrams relevant for the kinetic energy expansion. They are given by (87) and (88), with the only difference being that the sign of the $O(S^2)$ diagrams must be changed, since the corresponding coefficients $c_{ij}$, as given by (74), are equal to $-1$. To obtain the expansion to all orders of $S$, we have to multiply (78) by closed $ij$ loops of all powers resulting in a geometric progression. The kinetic energy per electron is thus given by:

$$\frac{T}{N} = \left[ T(0) + ST(a) \right] \left( 1 - S^2 + S^4 - S^6 + \cdots \right) = \frac{T(0) + ST(a)}{1 + S^2}. \quad (88)$$

If on the other hand we decide to first truncate the expansions of $\langle \Psi | T | \Psi \rangle$ and $\langle \Psi | \Psi \rangle$ to a particular order, say $S^2$, and then compute $T/N$, the result is:

$$\frac{T}{N} = \frac{T(0) + (n-1)S^2T(0) + ST(a)}{1 + nS^2}. \quad (89)$$

The difference between (88) and (89) is:

$$\delta T = (n-1)S^4 \frac{T(0) - T(a)/S}{1 + (n+1)S^2 + nS^4}, \quad (90)$$

which shows that if $(n-1)S^2 \sim 1$, the error in (89) is comparable to the leading order exchange term. In fact, if $n \to \infty$, (89) gives $T = NT(0)$, i.e. 100% error in the exchange energy. Even if the analysis is carried for a central pair and only its nearest neighbors, in a typical crystalline arrangement $n \sim 10$, so that there is a very stringent limitation on the allowed overlap, namely $S^2 \ll 1/n \sim 0.1$.

The diagrammatic formalism can also be used to examine the efficiency of dealing with the non-orthogonality problem by introducing a cut-off radius, $R_c$, for the one-particle functions, so that $f(r) = 0$ if $r > R_c$. If the desired accuracy is second order in overlap, we know that only energy terms corresponding to two-vertex diagrams such as

$$\ldots$$

need to be considered. However, with a cut-off approach, even if $R_c$ is chosen smaller than the nearest neighbor distance, one end up calculating (explicitly or implicitly) terms of higher than the required order in overlap, corresponding to diagrams such as:

$$\ldots$$

If the profile of the wavefunctions requires larger cut-off radius, the efficiency would diminish even further as terms corresponding to 3-point, 4-point, etc. loops, would now enter the calculations.

As a final example of application of the diagrammatic formalism, we will use it to gain insight into the physics underlying the linear scaling density functional theory developed by Mauri, Galli and Car, and by Ordejón et al. In this approach, non-orthogonal one-particle functions are used and the inverse of the overlap matrix, $S^{-1}$, entering the energy functional is replaced by a truncated series expansion:

$$S^{-1} \approx Q = \sum_{n=0}^{M} (I - S)^n,$$

where $I$ is the identity matrix, and $S$ has components $S_{ij}$. In addition, the following term is added to the energy functional:

$$\eta \left( N - \int d\tilde{r} \tilde{\rho}(r) \right), \quad (92)$$

where $\eta$ is a parameter that can be freely chosen, $N$ is the number of electrons in the system and $\tilde{\rho}(r)$ is the charge density computed with the truncated series expansion, Eq. (91). This method does not require explicit orthogonalization; a minimization of the energy functional of the non-orthogonal Kohn-Sham orbitals naturally leads also to orthogonalization.

Previously, the minimization procedure has been shown to be convergent when the expansion (91) is truncated at $M$ odd and $\eta$ is chosen to be positive. We can easily see the physical reason for this. In the diagrammatic language, an expansion of (91) to odd $M$ corresponds to considering only diagrams for the density expansion where the maximum number of solid lines (representing overlap integrals) is also odd. The expansion of the density, given by (57), shows that truncating the series (91) in this way introduces an error, which is equivalent to decreasing the electron charge density and the system becoming not neutral. The extra term added to the energy functional, (92), then represents the interaction energy between a positive external field and net positive charge. Thus, reducing this interaction energy to zero, i.e. energy minimization, is only achieved when orthogonality is attained.

With this physical picture in mind, it is easy to see that the method should also work when $M$ is chosen to be odd and the parameter $\eta$ negative. Indeed, in this case the error introduced by the truncated expansion (91) leads to increasing, not decreasing, electron charge. But with $\eta < 0$, this excess charge now interacts with a negative field and (92) is again positive definite. Realizing this without the physical picture in mind is not straightforward because the quantity $(Q - S^{-1})$, which is negative definite when $M$ is odd (see Ref. 13 for details), is not positive definite when $M$ is even.

We note that for an infinite periodic system with a net charge, the long-range Coulombic potential would in principle lead to divergent energy. In practice, the divergence can be removed by setting the $q = 0$ Fourier component of the interaction energy to zero – this is equivalent to adding a uniform potential and does not
VII. CONCLUSION

We have introduced a diagrammatic formalism for the calculation of normalized expectation values in terms of convergent series expansions in powers of one-particle overlap integrals. It can be applied to any order of overlap and for any spin configuration. The formalism has been introduced by analogy with conventional field theoretical methods; however it is applicable for systems with well-localized electrons. As a particular example, we have demonstrated energy calculations up to fourth order in overlap at the level of unrestricted Hartree-Fock and the valence-bond methods. The formalism presented here can give useful physical insight for the validity of other approaches, and potentially be used to improve their efficiency.

A possible extension of the formalism can include an analogy of skeletal diagrams and Dyson-like equations. This would be particularly useful in cases where there is a significant overlap among groups of electrons. In such cases, selected diagrams, accounting for the overlap among these electrons, could be summed to an infinite order. This possibility is illustrated with the example from the preceding section, Eq. (57).

The formalism can also be readily applied for localized bosons. The only difference with the fermionic case is in the sign of the diagrams as expected. For bosons, all loops carry a positive sign as a result of the commutation relations, however, in the construction of the linked-cluster expansion each chained loop still brings a negative sign. Therefore, in this case the sign of a diagram is given by $(-1)^{l-l_c}$ instead of $(-1)^{l-1}$, where $l-l_c$ is the number of closed loops not connected to external points.

VIII. ACKNOWLEDGMENTS

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10. Gauss’s theorem is not valid in 2-D, so it is not immediately apparent that the potential around the equilibrium positions is close to harmonic. But it can be seen if one considers a disk of positive uniform charge with radius $r_s$ around each electron. The electrostatic potential of such a disk at $r < r_s$ is $(4/\pi)r_sE(r/r_s)$, where $E$ is the complete elliptic integral of the second kind. The potential at $r > r_s$ is $4r_s\left[(r/r_s)E(r/r_s) - (r/r_s - r_s/r)K(r_s/r)\right]$, where $K$ is the complete elliptic integral of the first kind. If the elliptic integrals are expanded in power series, it can be established that close to the equilibrium position of a given electron, the potential due to the remaining electrons and all disks is approximately harmonic.
11. If the electrons are treated classically in the harmonic approximation with the potential obtained as outlined in [10], one obtains that $\sigma/r_s \approx r_s^{-1/4}$.
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