Nonorthogonal basis sets in quantum mechanics: Representations and second quantization

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A tensorial formalism is presented for the general use of nonorthogonal basis sets in quantum mechanics, both in representation theory and in second quantization. The natural formulation of second quantization for nonorthogonal basis sets defined here is shown to be formally very similar to the usual formulation for orthogonal basis sets. The formalism is used to study orthogonality effects in a Hubbard model defined on a semi-infinite lattice.

I. INTRODUCTION

In quantum mechanics the choice of a basis set is necessary both for the obtainment of concrete representation of vectors and operators in Dirac space,[1] and for the definition of them in Fock space.[2] The usual formulation of matrix representations and second quantization assumes the orthogonality of the chosen basis set, which, in principle, imposes no limitations and simplifies the associated algebra. Nevertheless, nonorthogonal basis sets have shown their utility in different areas of physics, such as quantum-field theory[3,4] on one hand, and molecular,[5] solid state,[6–8] and polymer[9] physics on the other: techniques like the linear combination of atomic orbitals (LCAO) allow the reduction of the state space to low dimensions, maintaining quality in the approximation. An evident way to take advantage of these properties is using the nonorthogonal basis set for defining the work subspace and orthogonalizing it afterwards. Another procedure widely used in molecular physics is to define matrix representations directly with the nonorthogonal basis carrying the overlap matrix along the equations.[10] The matrices obtained in this manner are not usual matrices in the sense that they do not transform normally under a change of basis; they correspond to objects defined in a space with a nonunitary metric.

However, there are situations where none of the previous procedures can be applied and where an extension of the formalism is required for the use of nonorthogonal basis sets. This is the case, for example, in the study of many-body effects in infinite or simply very large systems. For this, second quantization has proved to be an almost indispensable tool,[11] which imposes an orthogonal basis. For qualitative parametrized calculations it has been quite common to assume an orthogonal basis neglecting nonorthogonality effects.[12] Recently some methods have been developed where these effects are included in the Hamiltonian operator in an approximate manner.[8] However, a better approximation requires a correct treatment of the basis.

In this paper representation and second-quantization formalisms are extended to nonorthogonal basis sets by means of the introduction of the dual basis.[13,14] The implicit tensorial character of vectors and operators due to the nonorthogonality of the basis appears explicitly in the formalism and therefore will be incorporated in the notation. Although some of the concepts used in the present paper are already found in the literature (see Refs. 5 and 14 for representations, and Ref. 4 for second quantization), they are used for very specific tasks and in very specific contexts, the whole lacking uniformity and demanding a general scope formalization. The main contribution of this paper is the formalization of these preexisting handling to provide a flexible tool for directly using the nonorthogonal basis without the need of previous orthogonalization.

In Sec. II the dual basis is introduced leading to a tensorial representation formalism. Section III redefines second quantization by introducing different equivalent formulations of it. In Sec. IV the applicability of the formalism is shown with the study of nonorthogonality effects in the Hamiltonian of a semi-infinite one-dimensional Hubbard model.[15] After the conclusions in Sec. V, the Appendix includes the more cumbersome but necessary derivations and proofs of relations used throughout the paper.

II. DUAL BASIS AND TENSORIAL REPRESENTATIONS

$\mathcal{H}$ being the Hilbert space associated with a given physical system, we will have $\{|e_i\rangle\}$ denote a complete basis of it, denumerable, assuming the separability of $\mathcal{H}$. It is known[13] that there is a unique complete set of vectors $\{|e^i\rangle\}$ called dual basis that satisfies

$$\langle e^i|e_j\rangle=\langle e_i|e^j\rangle=\delta^i_j \ . \tag{1}$$

Using the completeness of both sets, it is very easy to obtain the closure relations

$$\sum_i |e_i\rangle\langle e^i|=\sum_i |e^i\rangle\langle e_i|=1 \ . \tag{2}$$

If a general vector $|\psi\rangle$ is expanded in the $\{|e_i\rangle\}$ basis with coefficients $c_{i\psi}$, the relationship

$$\langle e_j|\psi\rangle=\sum_i S_{ji}c_{i\psi} \tag{3}$$

will hold, $S_{ij}=\langle e_i|e_j\rangle$ being the metric of the $\{|e_i\rangle\}$ basis. Considering this metric as a finite matrix, one obtains

$$c_{i\psi}=\sum_i (\underline{S}^{-1})_{ij}\langle e_j|\psi\rangle \ . \tag{4}$$

The well-known closure relation for nonorthogonal basis sets[16] easily follows:

$$\sum_{i,j}|e_i\rangle(\underline{S}^{-1})_{ij}\langle e_j|=1 \ , \tag{5}$$

which helps us very nicely to obtain an explicit form for the dual basis defined in Eq. (1) by comparing both closure relations (2) and (5),

$$\langle e^i|=\sum_j (\underline{S}^{-1})_{ij}\langle e_j| \ , \tag{6a}$$

$$|e^i\rangle=\sum_j (\underline{S}^{-1})^*_{ij}|e_j\rangle \ . \tag{6b}$$

For later use it is interesting to know the relationship between the metrics of $\{|e_i\rangle\}$ and $\{|e^i\rangle\}$. It is straightforward to obtain it from (6), i.e.,

$$\langle e^i|e^j\rangle=(\underline{S}^{-1})_{ij} \ , \tag{7}$$

the first consequence being that if the direct basis $\{|e_i\rangle\}$ is normalized its dual basis will generally not be, unless $\{|e_i\rangle\}$ is orthonormal.

Given direct and dual basis, typical objects in the associated representation of the space state will be scalar products like $\langle e_i|\psi\rangle$, $\langle e^i|\psi\rangle$, $\langle e^i|H|e_j\rangle$, etc., $|\psi\rangle(H)$ being a general vector (operator) in $\mathcal{H}$. The way these objects transform under a change of basis reveals their tensorial character (see the Appendix). Hence, the introduction of tensorial algebra will be useful, allowing more transparency in our representation formalism.

Tensors are usually defined in the real domain, while in this case we need to work on the complex domain. The main difficulty is related to the anticommutativity of the scalar product defined in $\mathcal{H}$. To overcome it, we introduce what we call the property of the indexes: an index will be proper (improper) when referring to a ket (bra) of the direct basis or to a bra (ket) of the dual basis. Any use of the anticommutativity of the scalar product will be associated with a change in the property of the related indexes. We shall write improper indices with a bar on them. We can now denote the following objects in the form

$$\begin{aligned}
&\psi^i=\langle e^i|\psi\rangle, \quad H^i_j=\langle e^i|H|e_j\rangle \ , \\
&\psi_i=\langle\psi|e_i\rangle, \quad H_{\bar{i}\bar{j}}=\langle e_i|H|e_j\rangle \ , \\
&\psi_{\bar{i}}=\langle e_i|\psi\rangle, \quad H^{\bar{j}}_{\bar{i}}=\langle e_i|H|e^j\rangle \ , \\
&\psi^{\bar{i}}=\langle\psi|e^i\rangle, \quad H^{i\bar{j}}=\langle e^i|H|e^j\rangle \ ,
\end{aligned} \tag{8}$$

which are tensors of rank one or two. Upper (lower) indexes are associated with contravariance (covariance), as shown in the Appendix.

With the introduction of the metric tensors

$$S_{\bar{i}\bar{j}}=\langle e_i|e_j\rangle \ , \tag{9a}$$

$$S^{i\bar{j}}=\langle e^i|e^j\rangle \ , \tag{9b}$$

the handling of the formalism becomes very easy by simply making use of tensorial algebra and observing the rule that contractions will only be performed on indexes of the same property. The order in which tensors are written becomes irrelevant. Henceforth, for index contractions, the sum will be implied unless otherwise specified.

Depending on the type of tensors chosen to describe the system and quantum observables, different tensorial representations of $\mathcal{H}$ may be obtained, all equally valid. The relation between them can be easily obtained by means of the metric tensors. One possible choice is the widely used matrix representation that utilizes ψ^i and $H_{\bar{i}\bar{j}}$ for a vector and an operator in $\mathcal{H}$, respectively. In this representation, an eigenvector equation

$$H|\psi\rangle=\varepsilon|\psi\rangle \tag{10}$$

would appear as

$$H_{\bar{i}\bar{j}}\psi^j=\varepsilon S_{\bar{i}\bar{j}}\psi^i \ , \tag{11}$$

which is the same as

$$\underline{H}\underline{\psi}=\varepsilon\underline{S}\underline{\psi} \tag{12}$$

in the usual matrix notation.

What we shall call natural representation, consisting of a choice of tensors with indexes with the same property (for example, all proper), will be of special interest later. It avoids the appearance of metric tensors in the equations, making them formally identical to those obtained with the orthogonal basis-set formalism. The eigenvector equation will then be

$$H^i_j\psi^j=\varepsilon\psi^i \ . \tag{13}$$

The price to be paid for this is the loss of the hermiticity of H^i_j considered as a matrix, i.e., not $H^i_j=H^{j*}_i$, but rather $H^i_j=\overline{H}^{i*}_{\bar{j}}$. This is related to the fact that in the definition of H^i_j the operator is acting on elements of different basis sets (direct or dual) when acting on the ket or the bra. It represents, however, no special difficulty; moreover, it can be advantageous.[17] This natural representation will be very useful in the treatment of second quantization, as will be shown in Sec. III.

The flexibility of the tensorial formalism presented so far can be very useful in one-particle problems such as mean-field-like theories for atoms, molecules, and solids. See, for example, the case of infinite systems without full translational symmetry, where scatteringlike techniques based on Green's functions are widely used:[14,18] Both the explicit carrying of the overlap matrix or the orthogonalization of the basis are rather cumbersome tasks for these systems, whereas the choice of a suitable tensorial representation for the Hamiltonian and for the Green's function can reduce the computational effort considerably.

III. SECOND QUANTIZATION

From among the possible manners used in the introduction of the second-quantization formalism we have

chosen the following.

(i) From a given one-particle nonorthogonal basis set we generate the Fock space, obtaining a nonorthogonal basis set for the whole space and its correspondent dual basis.

(ii) We define creation and annihilation operators by defining their actuation on the basis, obtaining their commutation relations.

(iii) We study the Hermitian conjugation of the operators defined, obtaining annihilation and creation operators on the dual basis. The relations among them and their behavior under changes of basis will indicate the tensorial character of these operators.

(iv) At last we show the form of quantum-mechanical operators using the creation and annihilation operators defined.

A. Fock space, direct and dual basis

What we studied in Sec. II is valid for an arbitrary state space. Now we are dealing with the Fock space $\mathcal{F}$ associated with a bosonic or fermionic system: the main idea is to build a direct and dual basis of the whole space from the direct and dual basis of one-particle states. Let us then consider $\{|e_i\rangle\}$, the complete basis of the Hilbert space associated with one particle, $\mathcal{H}_1$, and its dual basis $\{|e^i\rangle\}$. It is easy to see that the set $\{|D_N^\alpha\rangle\}$ of all possible tensorial products conveniently symmetrized (antisymmetrized) of N one-particle basis vectors itself constitutes a complete basis of the Hilbert space of N bosons (fermions) $\mathcal{H}_N$. If $\{|e_i\rangle\}$ is not orthogonal, neither will $\{|D_N^\alpha\rangle\}$ be, both metrics being related through a generally complicated expression. If we now build the Fock space with the direct sum

$$\bigoplus_{N\geq 0} \mathcal{H}_N \ , \tag{14}$$

where $\mathcal{H}_0$ is the one-dimensional space generated by the vacuum vector $|0\rangle$, then trivially choosing this vector as the direct and dual basis of $\mathcal{H}_0$, the union

$$\bigcup_{N\geq 0} \{|D_N^\alpha\rangle\} \tag{15}$$

will be a basis of $\mathcal{F}$, nonorthogonal for vectors with the same number of particles and orthogonal for the others. The parallel building of a set union of dual basis sets gives the correspondent dual basis in $\mathcal{F}$. Hence, the explicit form of the vectors of both basis sets will be

$$|e_{i_1}\cdots e_{i_N}\rangle = \mathcal{N}\sum_P (\pm 1)^{\sigma_P} P\{|e_{i_1}\rangle\otimes\cdots\otimes|e_{i_N}\rangle\} \ , \tag{16a}$$

$$|e^{i_1}\cdots e^{i_N}\rangle = \mathcal{N}\sum_P (\pm 1)^{\sigma_P} P\{|e^{i_1}\rangle\otimes\cdots\otimes|e^{i_N}\rangle\} \ , \tag{16b}$$

with $\mathcal{N}=(N!)^{-1/2}$ for fermions, and $\mathcal{N}=(N!\prod_i n_i!)^{-1/2}$ for bosons, n_i being the number of times $|e_i\rangle$ appears in the sequence. Defined this way, they will generally not be normalized to unity, their norm squared consisting of an N-degree polynomial in the different scalar products between basis vectors of $\mathcal{H}_1$. The chosen normalization will allow the characterization of a change of basis in $\mathcal{F}$ by a simple linear combination of the creation and annihilation operators (see the Appendix), essential for obtaining a formalism parallel to the one for orthogonal basis sets. Although this nonunitary norm of the basis vectors has to be kept in mind, this will not affect the fundamental relations of the formalism. In the following sections we shall work with the occupation-number notation where a vector like the one defined in (16a) will appear as $|n_i\rangle$, while the correspondent of the dual basis (16b) will appear as $|n^i\rangle$.

B. Creation and annihilation operators

Let us define the creation and annihilation operators in the previously constructed Fock space. For doing this, we just need to define their actuation on the basis vectors. Using standard occupation-number notation, this definition reads

$$\begin{aligned} &\hat{a}_i|n_i\rangle=(n_i+1)^{1/2}|n_i+1\rangle \ , \\ &\hat{a}^i|n_i\rangle=n_i^{1/2}|n_i-1\rangle \end{aligned} \tag{17}$$

for boson creation and annihilation, respectively, and

$$\begin{aligned} &\hat{c}_i|n_i\rangle=(-1)^{\Sigma_i}(1-n_i)|n_i+1\rangle \ , \\ &\hat{c}^i|n_i\rangle=(-1)^{\Sigma_i}n_i|n_i-1\rangle \end{aligned} \tag{18}$$

for fermions, where Σ_i stands for the number of occupied one-particle states with indexes smaller than i. The notation for these operators is rather different from the usual one: instead of the $\dagger$ symbol, the position of the indexes is used to distinguish between creation and annihilation. One important reason for this is that these operators are not Hermitian conjugates of one another, as shall be shown. However, other notations are possible[19] that allow a better comparison with the usual formalism. The notation chosen is the best suited for the purposes of this paper, being the most transparent for the tensorial characteristics and manipulation.

Once defined, it is easy to obtain the familiar commutation and anticommutation relations between them,

$$\begin{aligned} &[\hat{a}_i,\hat{a}_j]=[\hat{a}^i,\hat{a}^j]=0 \ , \\ &[\hat{a}^i,\hat{a}_j]=\delta^i_j \end{aligned} \tag{19}$$

for bosons, and

$$\begin{aligned} &\{\hat{c}_i,\hat{c}_j\}=\{\hat{c}^i,\hat{c}^j\}=0 \ , \\ &\{\hat{c}^i,\hat{c}_j\}=\delta^i_j \end{aligned} \tag{20}$$

for fermions.

One of the major differences between the generalized formalism presented here and the one restricted to orthogonal basis sets arises when the Hermitian conjugation of the creation and annihilation operators is studied: the Hermitian conjugation of the creation (annihilation) operator does not result in the annihilation (creation) operator but rather in the annihilation (creation) operator defined on the dual basis, i.e.,

$$\begin{aligned} &(\hat{a}_i)^\dagger|n\rangle=n_i^{1/2}|n^i-1\rangle \ , \\ &(\hat{a}^i)^\dagger|n^i\rangle=(n_i+1)^{1/2}|n^i+1\rangle \end{aligned} \tag{21}$$

for bosons, and

$$(\hat{c}_i)^\dagger|n^i\rangle=(-1)^{\Sigma_i}n_i|n^i-1\rangle\ ,$$
$$(\hat{c}^{\,i})^\dagger|n^i\rangle=(-1)^{\Sigma_i}(1-n_i)|n^i+1\rangle \tag{22}$$

for fermions. This can be proven by showing that the relations

$$\langle n^i|\hat{a}^{\,i}|n_i'\rangle=(n_i')^{1/2}\delta_{n_i,n_i'-1}\ ,$$
$$\langle n_i'|(\hat{a}^{\,i})^\dagger|n^i\rangle=(n_i+1)^{1/2}\delta_{n_i',n_i+1}=(n')^{1/2}\delta_{n_i'-1,n_i} \tag{23}$$

hold for any vector of the direct and dual basis, when the occupations other than the ith are the same, while both matrix elements vanish when these occupations are different for the bra and the ket. Provided this, the completeness of both basis sets ensures the validity of the relation (21) for bosons. For fermions the proof is analogous.

Hence, we define the creation and annihilation operators on the dual basis of $\mathcal{F}$ for bosons as $\hat{a}^{\,\bar{i}}=(\hat{a}^{\,i})^\dagger$ and $\hat{a}_{\bar{i}}=(\hat{a}_i)^\dagger$, so that

$$\hat{a}^{\,\bar{i}}|n^i\rangle=(n_i+1)^{1/2}|n^i+1\rangle\ ,$$
$$\hat{a}_{\bar{i}}|n^i\rangle=n_i^{1/2}|n^i-1\rangle\ , \tag{24}$$

and similarly $\hat{c}^{\,\bar{i}}$, $\hat{c}_{\bar{i}}$ for fermions. Henceforth many relations will hold both for bosons and for fermions. Equations to appear for bosons will have their counterparts for fermions unless specified.

We can now define the number operator associated with a basis vector $|e_i\rangle$ as usually

$$\hat{n}_i|n_i\rangle=\hat{a}_i\hat{a}^{\,i}|n_i\rangle=n_i|n_i\rangle \tag{25}$$

(with no summation over i), where the hat has been put onto the operator to distinguish it from its eigenvalue. It should be noted that this operator is generally not Hermitian, its Hermitian conjugate being the number operator defined over the corresponding dual basis vector

$$\hat{n}_i^{\,\dagger}|n^i\rangle=(\hat{a}^{\,i})^\dagger(\hat{a}_i)^\dagger|n^i\rangle=n_i|n^i\rangle\ . \tag{26}$$

This nonhermiticity is a logical consequence of the nonorthogonality of the basis: This set of vectors cannot be thought of as being eigenvectors of any observable. Therefore, the question of how many particles are to be found in any of them has lost its sense. However, due to the way the creation and annihilation operators were defined, the eigenvalues of $\hat{n}_i$ and $\hat{n}_i^{\,\dagger}$ will be always integer numbers.

The total number operator N defined as

$$N=\hat{a}_i\hat{a}^{\,i} \tag{27}$$

does not change its form under a basis change (see the Appendix), which ensures its hermiticity. This property is guaranteed in this context by the orthogonality between basis vectors with a different number of particles, which makes the matrix elements

$$\langle D_\alpha^N|\hat{a}_i\hat{a}^{\,i}|D_\beta^M\rangle=M\langle D_\alpha^N|D_\beta^M\rangle\delta_{NM}=MS_{\alpha\beta}\delta_{NM}\ ,$$
$$\langle D_\beta^M|\hat{a}_i\hat{a}^{\,i}|D_\alpha^N\rangle^*=N\langle D_\beta^M|D_\alpha^N\rangle^*\delta_{NM}=NS_{\alpha\beta}\delta_{NM} \tag{28}$$

coincide.

C. Tensorial formulations

For a second quantization to be useful, the transformations of the creation and annihilation operators have to be algebraically simple when the one-particle basis set is changed. For orthonormal basis sets, the creation operator transforms like a ket of the one-particle basis, and the annihilation operator like a bra. The particular definitions of creation and annihilation operators given above have been chosen so as to behave satisfactorily under basis changes, generalizing what was explained for the orthonormal basis. In the Appendix these behaviors are studied and we arrive at the conclusion that $\hat{a}^{\,i}$ transforms like $\langle e^i|$, $\hat{a}_i$ like $|e_i\rangle$, $\hat{a}^{\,\bar{i}}$ like $|e^i\rangle$, and $\hat{a}_{\bar{i}}$ like $\langle e_i|$. Hence, as in Sec. II for representations, these behaviors show the tensorial character of these operators. Using the same conventions as in Sec. II, they can be assimilated to rank-one tensors: $\hat{a}^{\,i}$ contravariant proper, $\hat{a}_i$ covariant proper, $\hat{a}^{\,\bar{i}}$ contravariant improper, and $\hat{a}_{\bar{i}}$ covariant improper. Hermitian conjugation changes the property of indexes, just like complex conjugation does for vector representations. The notation used here is extremely transparent for basis changes and tensorial manipulations. Covariance and contravariance will be related through metric tensors, i.e.,

$$\hat{a}^{\,i}=S^{i\bar{j}}\hat{a}_{\bar{j}}\ ,$$
$$\hat{a}_i=S_{\bar{j}i}\hat{a}^{\,\bar{j}}, \tag{29}$$

relations derived in the Appendix that relate the annihilation (creation) operator on the direct basis with the one on the dual basis.

In the same way a nonorthogonal basis set gives rise to several possible tensorial representations, different choices of creation and annihilation operators generate what we shall call different formulations of the second quantization. The first introduced formulation at the beginning of this section, given by $\hat{a}_i$ and $\hat{a}^{\,i}$, will be called natural formulation, the index associated with both being proper. Its advantages are the commutation relations of Eqs. (19) and (20) and that the form of equations in this formalism is identical to those obtained for the orthonormal basis (as will be seen later). The price to be paid for this is that the hermiticity relation between the creation and annihilation operators does not hold. A formulation that includes this last characteristic is the one parallel to the matrix representation in Sec. II: choosing $\hat{a}_{\bar{i}}$ and $\hat{a}_i$ as the annihilation and creation operators, respectively. They are related through Hermitian conjugation, but they do not satisfy the commutations of Eqs. (19) and (20). Depending what properties are to be used, one formulation or the other should be chosen. The advantage of this formalism is that the transformation from one formulation to the other is rendered formally trivial by making use of the metric tensors to change the chosen creation and/or annihilation operators.

D. One- and two-particle operators

The explicit form that one- and two-particle operators will present in this formalism can be easily obtained from the known form of these operators when the basis is orthonormal, just by changing the orthonormal basis into a nonorthogonal one and making use of what was previously presented regarding basis changes in representations and in creation and annihilation operators. The resulting one-particle operator in the natural formulation reads

$$\hat{h}=h_{\nu}^{\mu}\hat{a}_{\mu}\hat{a}^{\nu}\ , \tag{30}$$

where the tensor h_{ν}^{μ} is the natural representation of the operator $\hat{h}$ in first quantization. Changing the basis otherwise, the matrix formulation is obtained:

$$\hat{h}=h_{\bar{\mu}\nu}\hat{a}^{\bar{\mu}}\hat{a}^{\nu}\ , \tag{31}$$

which, as can be seen,

$$\begin{aligned}h_{\nu}^{\mu}\hat{a}_{\mu}\hat{a}^{\nu}&=(h_{\bar{\sigma}\nu}S^{\bar{\sigma}\mu})(\hat{a}^{\bar{\delta}}S_{\mu\bar{\delta}})\hat{a}^{\nu}=h_{\bar{\sigma}\nu}\delta_{\bar{\delta}}^{\bar{\sigma}}\hat{a}^{\bar{\delta}}\hat{a}^{\nu}\\&=h_{\bar{\mu}\nu}\hat{a}^{\bar{\mu}}\hat{a}^{\nu}\ ,\end{aligned} \tag{32}$$

is related to the natural one simply by metric tensors. Two more possibilities are there, using the other two possible combinations of indexes.

There are 16 different forms for expressing the two-particle operator $\hat{V}$ as a result of the four indexes to be contracted. In the natural formulation its form is

$$\hat{V}=\tfrac{1}{2}V_{\sigma\delta}^{\mu\nu}\hat{a}_{\mu}\hat{a}_{\nu}\hat{a}^{\delta}\hat{a}^{\sigma}\ , \tag{33}$$

where the rank-four tensor $V_{\sigma\delta}^{\mu\nu}$ has the form

$$V_{\sigma\delta}^{\mu\nu}=(\langle e^{\mu}|\otimes\langle e^{\nu}|)\hat{V}(|e_{\sigma}\rangle\otimes|e_{\delta}\rangle)\ , \tag{34}$$

where the direct products imply no (anti)symmetrization. Using metric tensors we can obtain any other possible version. For example, for the matrix formulation we obtain

$$\hat{V}=(\tfrac{1}{2})V_{\bar{\mu}\bar{\nu}\sigma\delta}\hat{a}^{\bar{\mu}}\hat{a}^{\bar{\nu}}\hat{a}^{\delta}\hat{a}^{\sigma}\ , \tag{35}$$

which again can be obtained from the natural formulation by using metric tensors. These forms of the operators also make their invariance under basis changes explicit.

IV. EXAMPLE OF APPLICATION: HUBBARD HAMILTONIAN IN A SEMI-INFINITE CHAIN

As a simple application of the formalism we shall study the effects that the nonorthogonality of a local basis can introduce in a Hubbard Hamiltonian defined in a semi-infinite one-dimensional lattice. The Hubbard model[15] has been and continues to be much used in solid-state and recently in polymer physics as the simplest model that incorporates full many-body effects to study magnetism, superconductivity, etc.[12]

The model can be defined as follows. Given a fermionic system defined on a lattice, a local atomic basis $\{|e_i,\sigma\rangle\}$ is chosen as a one-particle basis set, where σ stands for the spin variable and i for the atomic site (assuming a single atomic orbital per atom, an s orbital, for example). The proposed Hamiltonian reads

$$H=U\sum_i n_{i\uparrow}n_{i\downarrow}+t\sum_{\langle i,j\rangle,\sigma}c_{i\sigma}^{\dagger}c_{j\sigma} \tag{36}$$

in the usual formalism, where $\langle i,j\rangle$ denotes nearest neighbors, U is the on-site biparticle Coulomb integral

$$U=\left\langle e_ie_i\left|\frac{1}{r_{12}}\right|e_ie_i\right\rangle\ , \tag{37}$$

and t is the nearest-neighbor hopping integral,

$$t=\langle e_i|T+V_{\text{ext}}|e_j\rangle\ , \tag{38}$$

for i and j nearest neighbors, assuming every other term is negligible. Orthogonality of the basis is implicitly assumed since the usual second quantization formalism is employed. Two main approximations have been made referring to a realistic system: the very limited basis and the consideration of extreme short-range interactions.

If the infinite system has full translational symmetry, U and t can be thought of as not varying with the site. However, if this symmetry is lacking they will generally be site dependent. Let us concentrate on the behavior of U. Two major factors will cause this dependence: on the one hand, the charge variations will alter the screening implicitly assumed in the neglect of all the other integrals and consequently will vary the value of U; on the other hand, the assumed basis orthogonality will make the basis element of one site depend on the other sites' disposition, altering again the U value. With the here-presented formalism we can study the latter effect.

As a typical case where these effects appear, let us consider the proposed semi-infinite chain that can be seen as the simplest case of a crystal surface or as a polymer chain end. Considering the actual nonorthogonal basis, we can think of the Hubbard Hamiltonian as written using the natural formulation of second quantization, where the two-body operator would read

$$\sum_i U_{ii}^{ii}n_{i\uparrow}n_{i\downarrow} \tag{39}$$

with $n_{i\uparrow}$ and $n_{i\downarrow}$ as number operators. Taking into account that the above expressed U integral is the one obtained for the direct basis elements, we see that

$$U=U_{\bar{i}\bar{i}ii} \tag{40}$$

can be assumed to be site independent if we do not consider the above-mentioned screening variation.

The analysis reduces to relating both tensorial forms of the same object. It is formally trivial using metric tensors. Calling $U(i)=U_{ii}^{ii}$, then

$$U(i)=U_{ii}^{ii}=S^{\bar{i}\bar{j}}S^{i\bar{k}}U_{\bar{j}\bar{k}ii}=(S^{\bar{i}\bar{i}})^2U\ , \tag{41}$$

where the diagonal elements of the metric tensor $S^{\bar{i}\bar{i}}$ are the only quantities to be calculated by means of an inversion of the overlap matrix. Considering for simplicity the only important overlap as being the one between nearest neighbors, s, by an iteration procedure one easily obtains $S^{\bar{i}\bar{i}}$ as a function of s and the site i. Introducing it in Eq.

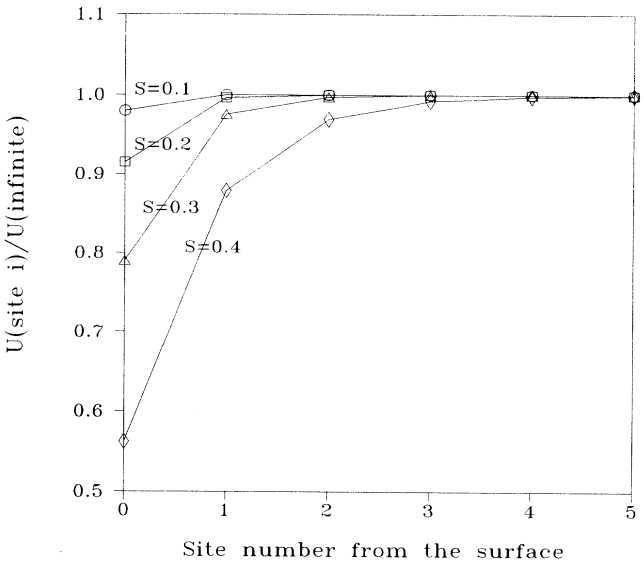

FIG. 1. Effective on-site Coulomb integral $U(i)$ as a function of the distance of the i site to the surface in units of the limiting value at infinite distance. The graphs corresponding to different values of the nearest-neighbor overlap s are presented.

(41), $U(i)$ is obtained. In Fig. 1 the results of $U(i)/U(\infty)$ are plotted versus site i for several values of s. These results show that the nonorthogonality effects tend to disappear quite rapidly when entering the bulk, but they can be quite important in the first sites, reducing the value of the integral that would enter the two-particle operator in the natural formulation of the Hamiltonian. In the orthogonal basis formalism the value of $U(i)$ would remain constant for every site. This would substantially alter the characteristics of the solutions at the surface, especially charge and spin arrangements at the outer sites of the chain. The effect of the decreasing of $U(i)$ due to the presence of the surface should be present in the model for a more realistic description of the system under study, as it is when a nonorthogonal basis is considered. The formalism proposed here includes this effect naturally, while, in the case of the usual orthogonal basis formalism, it has to be included in an *ad hoc* manner.

V. CONCLUSIONS

In this paper a general tensorial formalism for representations and second quantization using nonorthogonal basis sets has been presented. The dual basis is the key concept that allows the generalization and introduces the tensorial behaviors. By explicit construction of a basis in the Fock space from a one-particle basis, different possible formulations of the second quantization are obtained that relate to each other by metric tensor manipulations. The natural formulation is the one most similar to the formalism for orthogonal basis sets, maintaining commutation relations but not hermiticity relations between creation and annihilation operators.

As an application, the behavior of the on-site integral U in a semi-infinite one-dimensional Hubbard model is studied as a function of the site and the nearest-neighbor basis functions overlap, obtaining a substantial reduction of its value for the first sites of the chain.

The formalism can be used to extend all the existing many-body formalisms, especially Green's functions and perturbation theory, to nonorthogonal basis sets. This work is now in progress.

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APPENDIX: BASIS CHANGES AND TENSORIAL BEHAVIOR

In this appendix it will be shown how the tensors defined in the paper transform under basis changes, confirming the assumed tensorial character. The first question to consider is how the dual basis changes when the direct basis is changed. Let us then consider the two basis sets $\{|e_i\rangle\}$ and $\{|e_\mu\rangle\}$ with their respective metric matrices $\underline{S}$ and $\underline{R}$ and their respective dual basis sets $\{|e^i\rangle\}$ and $\{|e^\mu\rangle\}$. Let their relation be

$$|e_\mu\rangle=\sum_i(\underline{A})_{i\mu}|e_i\rangle\ , \tag{A1}$$

$(\underline{A})_{i\mu}$ being the matrix elements of the basis change matrix $\underline{A}$. The relation between both dual basis sets, according to Eqs. (3) and (6), will be

$$|e^\mu\rangle=\sum_{\nu,i,j}(\underline{S})_{ij}(\underline{A})_{j\nu}(\underline{R}^{-1})_{\nu\mu}|e^i\rangle\ , \tag{A2}$$

which can be significantly simplified when stating that

$$\underline{R}=\underline{A}^\dagger\underline{S}\underline{A}\ , \tag{A3}$$

and introducing it into Eq. (A2), one readily obtains the desired transform

$$|e^\mu\rangle=\sum_i(\underline{A}^{-1})^*_{\mu i}|e^i\rangle\ . \tag{A4}$$

Let us now consider the coefficients $\psi^i=\langle e^i|\psi\rangle$ of the expansion of a vector $|\psi\rangle$ in the basis $\{|e_i\rangle\}$. The way these objects transform when changing to the $\{|e_\mu\rangle\}$ basis can be easily obtained by making use of the closure relations of Eq. (2),

$$\psi^\mu=\sum_i(\underline{A}^{-1})_{\mu i}\psi^i\ . \tag{A5}$$

In the same way it can be seen how the objects $\psi_i=\langle\psi|e_i\rangle$ transform

$$\psi_\mu=\sum_i(\underline{A})_{i\mu}\psi_i\ . \tag{A6}$$

These last equations show that ψ_i transforms like a ket of the direct basis, which is called to be a rank-one covari-

ant tensor (and which is proper, following the criteria exposed in Sec. II), and that ψ^i transforms like a bra of the dual basis, i.e., contravariant (and also proper). That is the reason for the positioning of the indexes. If we rewrite the basis change matrix and its inverse in tensorial writing as follows,

$$\begin{aligned} A^{\,i}_{\mu} &= (\underline{A})_{i\mu} = \langle e^i | e_\mu \rangle \ , \\ A^{\,\mu}_{i} &= (\underline{A}^{-1})_{\mu i} = \langle e^\mu | e_i \rangle \ , \\ A^{\,\bar{i}}_{\bar{\mu}} &= (\underline{A})^{*}_{\mu i} = \langle e_\mu | e^i \rangle \ , \\ A^{\,\bar{\mu}}_{\bar{i}} &= (\underline{A}^{-1})^{*}_{i\mu} = \langle e_i | e^\mu \rangle \ , \end{aligned} \tag{A7}$$

the expression of the transformations showed above becomes an index contraction

$$\begin{aligned} \psi_\mu &= A^{\,i}_{\mu} \psi_i \ , \\ \psi^\mu &= A^{\,\mu}_{i} \psi^i \ . \end{aligned} \tag{A8}$$

Following this procedure we can obtain the tensorial character of the different scalar products involving one or two basis elements, like the examples shown in Eq. (8), and also of objects involving scalar products of tensorial products of basis elements, like the case of the biparticle integral of Eq. (34). The conclusion after following this procedure is the following rule: every ket (bra) of the direct basis that appears in the object to be characterized associates with a covariant proper (improper) index in the tensor, and every bra (ket) of the dual basis associates with a contravariant proper (improper) one. As stated in Sec. II, the handling of vectors and operators becomes the same as the handling of tensors with their usual rules, simply by observing that contractions are only possible between indexes of the same property. The basis-change tensors themselves enter the algebra as regular tensors; they are able to change their form to tensors two times covariant or contravariant just by making use of the metric tensors defined in Eqs. (9a) and (9b).

For the handling of the second-quantization operators and for the derivation of relations among them it is necessary to know how they transform under basis changes in the Fock space related to changes in the one-particle basis. Given two of these one-particle basis sets, $\{|e_i\rangle\}$ and $\{|e_\mu\rangle\}$, related by the tensor $A^{\,i}_{\mu}$, we construct the two-correspondent basis for the whole Fock space in order to define by them the correspondent creation and annihilation operators. With $\hat{a}$ operators we will refer in this section to both bosons and fermions because the results found here are equally valid for both. It can be shown (it is implicitly proven by Balian and Brezin[4]) that the relations between the two sets of operators are

$$\begin{aligned} \hat{a}_\mu &= A^{\,i}_{\mu} \hat{a}_i , \quad \hat{a}^{\,\mu} = A^{\,\mu}_{i} \hat{a}^{\,i} \ , \\ \hat{a}^{\,\bar{\mu}} &= A^{\,\bar{\mu}}_{\bar{i}} \hat{a}^{\,\bar{i}} , \quad \hat{a}_{\bar{\mu}} = A^{\,\bar{i}}_{\bar{\mu}} \hat{a}_{\bar{i}} \ , \end{aligned} \tag{A9}$$

i.e., they behave as the rank-one tensors described in Sec. III.

With the above results, the invariance of the total number operator N can be easily seen. For the natural formulation defined in Sec. III (for other formulations the derivation is the same),

$$N = \hat{a}_i \hat{a}^{\,i} = A^{\,\mu}_{i} A^{\,i}_{\nu} \hat{a}_\mu \hat{a}^{\,\nu} = \hat{a}_\mu \hat{a}^{\,\mu} \ . \tag{A10}$$

At last, we present the proof of Eq. (29) in Sec. III that relates different tensorial forms of the creation and annihilation operators, not only because of its utility, but also because with the same technique many other relations can be derived, by assuming a nonorthogonal basis $\{|e_i\rangle\}$ and an orthogonal one $\{|e_\mu\rangle\}$. For the latter we know that

$$|e^\mu\rangle = |e_\mu\rangle \ , \tag{A11}$$

and then, just by transforming and backtransforming [because of the use of Eq. (A11) summations are presented explicitly]

$$\begin{aligned} \hat{a}_i &= \sum_{\mu} \langle e_\mu | e_i \rangle \hat{a}_\mu \\ &= \sum_{\mu, j} \langle e_j | e_\mu \rangle \langle e_\mu | e_i \rangle \hat{a}^{\,\bar{j}} \\ &= \sum_{j} \langle e_j | e_i \rangle \hat{a}^{\,\bar{j}} \ , \end{aligned} \tag{A12}$$

which is the same as

$$\hat{a}_i = S_{\bar{j}i} \hat{a}^{\,\bar{j}} \ . \tag{A13}$$

For the other relations the derivation is the same.

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[1]C. Cohen-Tannoudji, B. Diu, and F. Laloë, *Mécanique Quantique* (Hermann, Paris, 1977), Chap. II.

[2]E. Merzbacher, *Quantum Mechanics,* 2nd ed. (Wiley, New York, 1970), Chap. 20.

[3]See, for example, for coherent-state representations, L. H. Schulman, *Techniques and Applications of Path Integration* (Wiley, New York, 1981), pp. 242–258.

[4]R. Balian and E. Brezin, Nuovo Cimento B **64**, 37 (1969).

[5]R. Hoffmann, J. Chem. Phys. **39**, 1397 (1963); S. S. Sung and R. Hoffmann, J. Am. Chem. Soc. **107**, 578 (1985).

[6]D. J. Chadi, Phys. Rev. B **16**, 3572 (1977); E. O. Kane, *ibid.* **13**, 3478 (1976).

[7]J. A. Vergés, and F. Ynduráin, Phys. Rev. B **37**, 4333 (1988).

[8]P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950); P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983); J. A. Majewski and P. Vogl, Phys. Rev. Lett. **57**, 1366 (1986); Phys. Rev. B **35**, 9666 (1987); F. Flores, A. Martín-Rodero, E. C. Goldberg, and J. C. Durán, Nuovo Cimento **10**, 303 (1988).

[9]A. Karpfen and J. Petkov, Solid State Commun. **29**, 251 (1979).

[10]J. P. Lowe, *Quantum Chemistry,* (Academic, New York, 1979), Chap. 9.

[11]L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[12]G. Treglia, F. Ducastelle, and D. Spanjaard, Phys. Rev. B **21**, 3729 (1980); J. E. Hirsch, S. Tang, E. Loh, and D. J. Scalapino, Phys. Rev. Lett. **60**, 1688 (1988); L. Miláns del Bosch and F. Guinea, (unpublished).

[13]V. V. Voevodin, *Linear Algebra* (Mir, Moscow, 1982), p. 262.

[14]D. Vanderbilt and J. D. Joannopoulos, Phys. Rev. B **22**, 2927 (1980).

[15]J. Hubbard, Proc. R. Soc. (London) Ser. A **276**, 283 (1963).

[16]P.-O. Löwdin, Int. J. Quantum Chem. **2**, 867 (1968), and references therein.

[17]J. D. Weeks, P. W. Anderson, and A. G. H. Davidson, J. Chem. Phys. **58**, 1388 (1973).

[18]P. Ordejón, E. Martínez, and F. Ynduráin, Phys. Rev. B **40**, 12 416 (1989); E. Artacho and F. Ynduráin, *ibid.* **42**, 11 310 (1990).

[19]A possible alternative notation for the operators would be $\hat{a}^{i}$ and $\hat{a}_{i}^{\dagger}$ for annihilation and creation operators on the direct basis, respectively, and $\hat{a}_{\bar{i}}^{\dagger}\,(=\hat{a}_{i})$ and $\hat{a}^{\bar{i}}\,(=\hat{a}^{i\dagger})$ for annihilation and creation operators on the dual basis. It has the advantage of reducing to the ordinary notation for the orthogonal basis when the position of the index is disregarded. Moreover, this notation for the natural formulation is very similar to the usual one for orthogonal basis sets. It is, however, not as suited for the general formalism as the notation introduced in Sec. III because of the appearance and disappearance of †'s with the changes in the property of the indexes. For example, Eq. (29) would read $\hat{a}^{i}=S^{i\bar{j}}\hat{a}_{\bar{j}}^{\dagger}$ and $\hat{a}_{i}^{\dagger}=S_{\bar{j}i}\hat{a}^{\bar{j}}$.