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Electron Pair Methods *vs.* Independent Particle Approximation: Quasiparticle Transformations

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Some basic algebraic features of quasiparticle transformations are reviewed. Special nonlinear quasiparticle transformations are introduced leading to the second quantized counterparts of geminal-type (correlated) wave functions. Algebraic representations of strong and weak orthogonality are discussed, and these issues are generalized to the case of non-orthogonal basis sets leading to the concepts of strong and weak biorthogonality.

I. ONE-PARTICLE TRANSFORMATIONS

As introduction, we shall give a brief overview of linear quasiparticle transformations, a standard tool in quantum chemistry and solid state physics[1].

Given a set of orthonormalized orbitals $\{\varkappa_\mu\}$, the corresponding creation ($\varkappa_\mu^+$) and annihilation ($\varkappa_\mu^-$) operators obey the fermion anticommutation rules

$$[\chi_\mu^+, \chi_\nu^+]_+ = [\chi_\mu^-, \chi_\nu^-]_+ = 0 \tag{1a}$$

$$[\chi_\mu^+, \chi_\nu^-]_+ = \delta_{\mu\nu} \tag{1b}$$

Operators $\varkappa_\mu^+$ ($\varkappa_\mu^-$) create (annihilate) an electron on orbital $\varkappa_\mu$. The creation and annihilation operators are adjoints of each other.

Transformation of the elementary fermion operators $\varkappa_\mu^+$ and $\varkappa_\mu^-$ leads to new operators creating and annihilating »quasiparticles«. Such transformations can be called quasiparticle transformations.

Consider a general linear transformation

$$\psi_i^+ = \sum_\mu (A_{i\mu}\, \chi_\mu^+ + B_{i\mu}{}^*\, \chi_\mu^-) \tag{2a}$$

$$\psi_i^- = \sum_\mu (A_{i\mu}{}^*\, \chi_\mu^- + B_{i\mu}\, \chi_\mu^+) \tag{2b}$$

the asterisks indicating complex conjugates. Algebraic properties of the transformed operators are defined by their commutation rules which can be derived by substituting Eqs. (2) into the relevant commutators:

$$[\psi_i^+, \psi_k^+]_+ = \sum_\mu (A_{i\mu}\, B_{k\mu}{}^* + B_{i\mu}{}^*\, A_{k\mu}) \tag{3a}$$

$$[\psi_i^-, \psi_k^-]_+ = \sum_\mu (A_{i\mu}{}^*\, B_{k\mu} + B_{i\mu}\, A_{k\mu}{}^*) \tag{3a}$$

$$[\psi_i^+, \psi_k^-]_+ = \sum_\mu (A_{i\mu} A_{k\mu}^* + B_{i\mu}^* B_{k\mu}) \tag{3a}$$

Transformation (2) is said to be canonical if the transformed fermion operators obey the same commutation properties as the untransformed ones to:

$$[\psi_i^+, \psi_k^+]_+ = [\psi_i^-, \psi_k^-]_+ = 0 \tag{4a}$$

$$[\psi_i^+, \psi_k^-]_+ = \delta_{ik} \tag{4b}$$

It is seen from Eq. (3) that the general transformation (2) is canonical if certain conditions for thansformation coefficients A and B are satisfied. Namely, in matrix notations:

$$A\, B^+ = 0 \tag{5a}$$

$$(A\, A^+ + B\, B^+) = 1 \tag{5b}$$

where the dagger indicates the adjoint of the matrix. Eqs. (5) are sufficient conditions for transformation (2) to be a canonical transformation.

It is to be emphasized that operator ψ_i^+ does not generally create an electron; it creates a quasiparticle. Such quasiparticles are widely applied in theoretical physics to describe elementary excitations and similar quantum phenomena[2]. Second quantization is essential to describe the mathematical properties of quasiparticles and to deal with them.

Three important special cases of the general quasiparticle transformation in Eq. (2) are to be distinguished.

(i) If all the coefficients B are zero, Eq. (2) reduces to a simple linear transformation of the orbital space:

$$\psi_i^+ = \sum_\mu A_{i\mu}\, \chi_\mu^+ \tag{6a}$$

$$\psi_i^- = \sum_\mu A_{i\mu}^*\, \chi_\mu^- \tag{6b}$$

This is not really a quasiparticle transformation since ψ_i^+ creates and electron on the transformed orbital ψ_i. The canonical condition of Eq. (5a) is automatically fulfilled while (5b) reduces to

$$A\, A^+ = 1$$

that is, matrix A should be unitary in order to Eq. (6) to be a canonical transformation preserving the commutation rules.

(ii) If all coefficients A are zero, we have

$$\psi_i^+ = \sum_\mu B_{i\mu}^*\, \chi_\mu^- \tag{7a}$$

$$\psi_i^- = \sum_\mu B_{i\mu}\, \chi_\mu^+ \tag{7b}$$

It is seen that the role of creation and annihilation operators is reversed by transformation (7). One can say that operator ψ_i^+ (ψ_i^-) creates (annihilates) a hole. Eq. (7) is called a particle — hole transformation[3,4].

(iii) In general, Eq. (2) mixes together particle- and hole-creation operators. Transformation of this type are called Boguliobov transformations and are often utilized in the theory of superconductivity and superfluidity[1].

II. TWO-PARTICLE TRANSFORMATIONS

We turn now to a less standard chapter in the theory of quasiparticle transformations which are non-linear in fermion operators. The aim of the present paper is to discuss some formal freatures of the two-electron transformation of the following form:

$$\psi_i^+ = \sum_{\mu<\nu} C_{\mu\nu}{}^i \chi_\mu{}^+ \chi_\nu{}^+ \tag{8a}$$

$$\psi_i^- = \sum_{\mu<\nu} C_{\mu\nu}{}^i \chi_\nu{}^- \chi_\mu{}^- \tag{8b}$$

where the summation restriction $\mu < \nu$ avoids double counting of electron pairs. Coefficients $C_{\mu\nu}{}^i$ are assumed to be real.

Algebraic properties of the transformed operators are quite interesting[5]. By substitution, the following commutation rules are found:

$$[\psi_i^+, \psi_k^+]_- = [\psi_i^-, \psi_k^-]_- = 0 \tag{9a}$$

$$[\psi_i^+, \psi_k^-]_- = Q_{ik} \tag{9b}$$

where operators Q_{ik} are defined as

$$Q_{ik} = \sum_{\mu<\nu} C_{\mu\nu}{}^i C_{\mu\nu}{}^k + \sum_{\mu\nu\lambda} C_{\mu\lambda}{}^i C_{\nu\lambda}{}^k \chi_\mu{}^+ \chi_\nu{}^- \tag{10}$$

where the convention $C_{\mu\nu}{}^i = -C_{\nu\mu}{}^i$ is introduced. The first thing we realize is that we have commutators, instead of anticommutators, in Eqs. (9). This is quite natural since ψ^+ (ψ^-) creates (annihilates) a pair of electrons. The relevant quasiparticles are, therefore, bosons.

Next, operators Q_{ik} are to be discussed. If one deals with elementary bosons, δ_{ik} should stand in replacement of Q_{ik}. The presence of Q_{ik} reflects the composite nature of the bose quasiparticles[1,5–10]. Operators Q_{ik} in the form of Eq. (10) complicate tremendously the algebra of the quasiparticles. Since Q_{ik} is a matrix of operators, it is hard to find an efficient theory for dealing with them. Under certain conditions, however, the structure of the quasiparticle commutators can be simplified leading to a practically applicable theory.

The first simplification arises if one requires the geminals (two-electron wave functions) to be orthogonal to each other:

$$\langle \text{vac} | \psi_i^- \psi_k^+ | \text{vac} \rangle = \delta_{ik} \tag{11}$$

This equation is the second quantized representant of the so called »weak orthogonality« condition which is commonly expressed as

$$\int \psi_i (x_1, x_2)\, \psi_k (x_1, x_2)\, dx_1\, dx_2 = \delta_{ik} \tag{11'}$$

Substituting the quasiparticle transformation from Eqps. (8) into Eq. (11), one gets the weak orthogonality condition in terms of coefficients

$$\sum_{\mu<\nu} C_{\mu\nu}{}^i C_{\mu\nu}{}^k = \delta_{ik} \tag{12}$$

By this result, the quasiparticle operators of Eq. (5) under weak orthogonality take the form

$$Q_{ik} = \delta_{ik} + \sum_{\mu\nu\lambda} C_{\mu\lambda}{}^{i}\, C_{\nu\lambda}{}^{k}\, \chi_{\mu}{}^{+}\, \chi_{\nu} \tag{13}$$

This apparent simplification, as compared to Eq. (10), does not make the algebra of quasiparticle operators much simpler, since one still cannot transpose different creation and annihilation operators. However, it has the interesting feature

$$Q_{ik} \,|\, \mathrm{vac}\rangle = \delta_{ik} \,|\, \mathrm{vac}\rangle \tag{14}$$

This means that the quasiparticle operator ψ_i^- is a true annihilator with respect to ψ_i^+ since

$$\psi_i^- \psi_i^+ |\, \mathrm{vac}\rangle = (1 + \psi_i^+ \psi_i^-) \,|\, \mathrm{vac}\rangle = |\, \mathrm{vac}\rangle.$$

As mentioned above, the main problem consists of transposing ψ_i^+ and ψ_k^- for $i \neq k$. This difficulty can be handled under the so called »strong orthogonality« requirement which is commonly given as

$$\int \psi_i (x_1, x_2)\, \psi_k (x_1, x_2)\, dx_1 = 0 \quad \text{for} \quad i \neq k \tag{15}$$

In terms of coefficients the same condition writes

$$\sum_{\mu} C_{\mu\nu}{}^{i}\, C_{\mu\lambda}{}^{k} = 0 \quad \text{for } i \neq k \tag{16}$$

Using Eq. (16), the quasiparticle commutators under strong orthogonality become

$$Q_{ik} = \delta_{ik} \,[1 + \sum_{\mu\nu\lambda} C_{\mu\lambda}{}^{i}\, C_{\nu\lambda}{}^{k}\, \chi_{\mu}{}^{+}\, \chi_{\nu}] \tag{17}$$

which is an essential simplification, as compared to Eq. (10) or Eq. (13), since it enables algebraic manipulation *e. g.*

$$\psi_i^- \psi_k^+ \,|\, \mathrm{vac}\rangle = \delta_{ik} \,|\, \mathrm{vac}\rangle \tag{18}$$

where Eq. (14) was also used.

It is to be noted here that commutators Q_{ii} at the diagonal cannot be eliminated from the theory: they reflect the physical fact that the Bose-type particles in question are composite quasiparticles.

The essential importance of strong orthogonality resulting in Eq. (17) lies in the fact that it results in exactly the same algebra as that for elementary bosons. Operators Q_{ii} do not enter the formalism when calculating matrix elements, and any standard rules (Wick's theorem, etc.) remain valid. A natural form of an N-electron wave function can be written as

$$\Psi = \psi_1^+ \psi_2^+ \cdots \psi^+_{N/2} \,|\, \mathrm{vac}\rangle \tag{19}$$

which is a straightforward generalization of the Hartree-Fock single determinantal wave function

$$\Psi_{\mathrm{HF}} = \chi_1^+ \chi_2^+ \cdots \chi_N^+ \,|\, \mathrm{vac}\rangle \tag{20}$$

while Eq. (20) corresponds to the model of independent electrons, Eq. (19) specifies the model of independent pairs. (We mention only in passing that the internal structure of composite particles can be affected by interpair, *e. g.* inductive, interactions[5–8].)

The formal analogy between one-electron models and geminal-type schemes was realized a long time ago.[11–13] The present discussion based on the second quantized formalism sheds some more light onto this connection, emphasizing the algebraic importance of the strong orthogonality condition.

Strong orthogonality can be ensured in two ways. (i) Either as an auxiliary condition at the variational determination of coefficients $C_{\mu\nu}^{i}$, or (ii) by expanding the geminals in mutually exclusive orthogonal subspaces. Way (i) is essentially the method of antisymmetrized product of strongly orthogonal geminals (APSG)[14], while (ii) results in strictly localized geminals (SLG).[5-8] As it was shown by Arai[15], these two ways are mathematically equivalent since for an APSG-type wave function there exists a transformation of the underlying one-electron basis set so that the transformed basis functions obey the condition of point (ii).

III. THE NON-ORTHOGONAL CASE

In practical applications, one is often faced with the problem that the original basis of one-electron functions $\{\chi\}$ is not orthonormalized. The relevant anticommutation rules for fermion operators are then read[1,5,7,16,17]

$$\{\chi_\mu^+, \chi_\nu^+\}_+ = \{\chi_\mu^-, \chi_\nu^-\}_+ = \{\tilde{\chi}_\mu^-, \tilde{\chi}_\nu^-\}_+ = 0$$

$$\{\chi_\mu^+, \chi_\nu^-\}_+ = S_{\mu\nu} \tag{21}$$

$$\{\chi_\mu^+ \tilde{\chi}_\nu^-\}_+ = \delta_{\mu\nu}$$

where $\chi_\nu^- \equiv (\chi_\nu^+)^\dagger$ but the true annihilation operators $\tilde{\chi}_\nu^-$ are not adjoints of χ_ν^+. Instead, the following relation holds:

$$\tilde{\chi}_\nu^-, = \sum_\lambda S_{\nu\lambda}^{-1} \chi_\lambda^- \tag{22}$$

Using creation operators χ_μ^+ and annihilation operators $\tilde{\chi}_\nu^-$ one works in the same algebra as in the orthogonal case. The non-orthogonality is reflected by the fact that the adjoin relation does not hold. This leads to certain difficulties in evaluating matrix elements which can be most conveniently solved by consistent use of the biorthogonal formalism.[5] Anyway, since the basic algebraic rule are preserved, the quasiparticle transformations discussed in Sect. II. can easily be generalized to the non-orthogonal case mutatis mutandis. The basic transformation of Eq. (8) becomes

$$\psi_i^+ = \sum_{\mu<\nu} C_{\mu\nu}^{i} \chi_\mu^+ \chi_\nu^+ \tag{23a}$$

$$\tilde{\psi}_i^- = \sum_{\mu<\nu} C_{\mu\nu}^{i} \tilde{\chi}_\nu^- \tilde{\chi}_\mu^- \tag{23b}$$

The transformed quasi-boson operators obey the commutation rules exactly in the same form as given in Eq. (9), while the quasiparticle commutator in the general case is given by

$$Q_{ik} = \sum_{\mu<\nu} C_{\mu\nu}^{i} C_{\mu\nu}^{k} + \sum_{\mu\nu\lambda} C_{\mu\lambda}^{i} C_{\nu\lambda}^{k} \chi_\mu^+ \tilde{\chi}_\nu^- \tag{24}$$

As a generalization of the weak orthogonality defined in Eq. (11), one can formulate the requirement of »weak bi-orthogonality« as

$$\langle \mathrm{vac} \,|\, \tilde{\psi}_i^- \psi_k^+ \,|\, \mathrm{vac} \rangle = 0 \quad (i \neq k) \tag{25}$$

which, in terms of coefficients $C_{\mu\nu}^{i}$, leads again to the same expression of Eq. (12). Consequently, the quasiparticle commutator under weak biorthogonality simplifies to

$$Q_{ik} = \delta_{ik} + \sum_{\mu\nu\lambda} C_{\mu\lambda}^{\ i} C_{\nu\lambda}^{\ k} \chi_{\mu}^{+} \tilde{\chi}_{\nu}^{-} \tag{26}$$

Further simplification is possible by requiring the »strong bi-orthogonality« of ψ and $\tilde{\psi}$, which results again in Eq. (16) for the coefficients. The quasiparticle commutator reduces to

$$Q_{ik} = \delta_{ik} [1 + \sum_{\mu\nu\lambda} C_{\mu\lambda}^{\ i} C_{\nu\lambda}^{\ k} \chi_{\mu}^{+} \tilde{\chi}_{\nu}^{-}] \tag{27}$$

which is the generalization o. Eq. (17).

IV. CONCLUSIONS

In this paper we aimed to review the second quantized representation of geminal type wave functions, using the language of quasiparticle transformations. The formal similarity between the wave functions of idependent electron models and those of separated pair theories was studied. It was shown that these two models can be described by the same algebraic structure provided that strong orthogonality is fulfilled for the geminals in orthonormalized metrics. If the basis set is overlapping, a biorthogonal formulation turns out to be conveninent and one can define strong and weak biorthogonality. In this case the algebra of quasiparticles is similar to the algebra of electrons if the strong biorthogonality condition is fulfilled. The formal considerations of this paper are useful theoretical backgrounds of the applications to chemical bond theories[5] as well as various geminal type models such as APSG[11-14].

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REFERENCES

1. P. R. Surján, *Second Quantized Approach to Quantum Chemistry,* Springer, Heidelberg, 1989.
2. L. D. Landau, E. M. Lifsic, and L. P. Pitajevskij, *Theoretical Physics Vol.* **9** (Stat. Phys. 2), Akademie Verlag, Berlin (1980).
3. A. D. McLahlan, *Mol. Phys.* **4** (1961) 49.
4. H. C. Longuet-Higgins in: *Quantum Theory of Atoms, Molecules and the Solid State,* Ed. Lowdin P. O., Academic, New York p 105 (1966).
5. P. R. Surján in: *Theoretical models of chemical bonding,* Ed. Z. B. Maksić, Springer, Heidelberg, (1989).
6. P. R. Surján, *Phys. Rev.* **A90** (1984) 48.
7. P. R. Surján, I. Mayer, and I. Lukovits, *Phys. Rev.* **A32** (1985) 749.
8. P. R. Surján, *Croat. Chem. Acta* **57** (1984) 833.
9. M. Girardeau, *J. Math. Phys.* **4** (1963) 1096; *Phys. Rev. Lett.* **27** (1971) 822; *Int. J. Quantum Chem.* **17** (1980) 25.
10. V. Kvasnicka, *Czech. J. Phys.* **B32** (1982) 947; *Croat. Chem. Acta* **57** (1984) 1643.
11. A. C. Hurley, J. E. Lennard-Jones, and J. A. Pople, *Proc. Roy. Soc.* **A220** (1953) 446.
12. J. M. Parks, and R. G. Parr, *J. Chem. Phys.* **28** (1958) 335.

13. (a) W. Kutzelnigg, *J. Chem. Phys.* **40** (1964) 3640, (b) E. Kapuy, *Chem. Phys. Letters* **3** (1969) 43; *Theor. Chim. Acta* **6** (1966) 281; *Acta Phys. Hung.* **27** (1969) 179; (c) C. Valdemore, *Phys. Rev. A* **18** (1978) 2443; **31** (1985) 2114, 2123; **33** (1986) 1525.

14. R. Ahlrichs and W. Kutzelnigg, *J. Chem. Phys.* **48** (1968) 1819.

15. T. Arai, *J. Chem. Phys.* **33** (1960) 95.

16. I. Mayer, *Int. J. Quantum Chem.* **23** (1983) 341.

17. B. Ng and D. J. Newman, *J. Chem. Phys.* **83** (1985) 1758.

SAŽETAK

Metoda elektronskih parova vs. približenje nezavisnih čestica: Kvazičestične transformacije

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Prikazana su neka osnovna svojstva kvazičestičnih transformacija. Uvedene su nelinearne kvazičestične transformacije koje daju korelirane valne funkcije geminalnog tipa. Razmatrana je koncepcija jake i slabe biortogonalnosti.