QUASIPARTICLE APPROACH TO THE ELECTRONIC STRUCTURE OF MOLECULES

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A quasiparticle approach to the electronic structure of molecules is developed in full analogy with the quasiparticle theory of nuclear structure[1-3]. It seems that a canonical transformation of the Hartree-Fock type with complex coefficients represents a natural quasiparticle transformation in the description of molecules. Only in the projected version of this model, in which the variational trial function is the real part of a complex Slater determinant, dominant electron correlations are parametrized satisfactorily. Since the projection operator (Re) is trivial in this case, a very simple secular equation is derived by energy minimization.

Numerical results demonstrate that this simple model is able to describe about two thirds of the electron correlations found by the large-scale configuration mixing calculations in which several thousands of Slater determinants are used[4]. It has also been demonstrated that this model represents a natural unification of classical theories of chemical bonds - the molecular-orbital method and the valence-bond method[5].

References

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