On the Restricted and Combined Use of Rüdenberg's Approximations in Crystal Orbital Theories of Hartree-Fock Type

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The analysis based on Rüdenberg's well-known letter of 1951, which has been outlined for molecules in a preceding contribution, has now been transfered to translational periodic systems in one, two, or three dimensions. Entitled "On the Three- and Four-Center Integrals in Molecular Quantum Mechanics", this letter explicitly presents two approximations only for four-center repulsion integrals. When applied to some types of three-center repulsion integrals, however, these two recipes still imply considerable oversimplifications. Using both one-electron and two-electron routes of Rüdenberg's expansion, such shortcomings can be avoided strictly. Starting from a simple "Unrestricted and Combined" (U&C) approximation scheme introduced elsewhere, an improved "Restricted and Combined" (R&C) approximation picture for Fock-matrix elements now will be outlined, which does not tolerate any unnecessary oversimplifications. Although the simplicity of the U&C scheme is lost in this case, R&C-approximated Fock-matrix elements still can be constructed from one- and two-center integrals alone in an effective way. Moreover, due to their dependence on a single geometric parameter, all types of two-center integrals can be calculated in advance for about one hundred fixed interatomic distances at the desired level of sophistication, and stored once and for all. A cubic spline algorithm may be taken to interpolate the actual integral value from each precomputed list.

Key words: Unrestricted (and Restricted) Hartree-Fock Crystal Orbitals; Integral Approximations According to Rüdenberg; Extended Hückel Theory (EHT).