06.2-01 THE EXACT EVALUATION OF ELECTRON DENSITY. By C.L. Davis and E.N. Maslen, Crystallography Centre, University of Western Australia, Nedlands, Western Australia.

Electron densities can be evaluated from analytical solutions to the many-particle Schrodinger equation. The solutions, which are in the form of perturbation expansions, are exact in the sense that they can be made arbitrarily close to the correct solution by taking sufficient terms in the expansion. The algebra is straightforward, and the expansions converge rapidly for the systems of major interest. It is expected that study of the asymptotic behaviour of the expansions will lead to further simplifications in their analytical form.

For many-electron wavefunctions where the nuclei are regarded as infinitely heavy the perturbation parameter relates directly to the electron correlation energy. The first order perturbation equation

$$(H_o - E_o)F = (E_1 - V)\Psi_o \qquad (1)$$

has infinitely many solutions F. These solutions can be expressed as products of polynomials and other simple functions of the electron coordinates. There are discontinuities in the analytical form of the solution at boundary surfaces in the electron coordinate space.

The essential task is to extract from the infinite number of solutions that one which is both normalizable and preserves the hermiticity of the Hamiltonian operator, in which case

$$F = \Psi_1. \qquad (2)$$

Ψ_1 is the first order correction to the wavefunction.

The hermiticity condition is more restrictive than requiring that F be locally square integrable at the singular points in the potential. It also requires that F be continuous and smooth across the boundary surfaces at which its analytical form changes. A systematic method for meeting these requirements provides the solution in its physically acceptable form. This is possible only when E_1 has the particular value

$$E_1 = \langle\Psi_o|V|\Psi_o\rangle \qquad (3)$$

The extension to higher order perturbation terms changes coefficients in algebraic expansions on the right hand side of equation (1). The method of solution for the higher order equations is unchanged.

When nuclear motion is included the first order equation becomes

$$(H_o - E_o)G = (E_1 - \Delta H)\Psi_o \qquad (4)$$

where the perturbing term ΔH includes Laplacian kinetic energy operators for the nuclei. The coefficients multiplying the Laplacian operators are inversely proportional to the mass M for each nucleus. M^{-1} may be regarded as the perturbation parameter. The derivatives in the Laplacian change powers and coefficients in the function Ψ_o, without radically altering its form. The method of solution is similar to that when ΔH contains potential terms only, except that (3) is not valid when kinetic energy terms are included. The values for E_1 are determined as part of the solution.

Model systems studied so far include the ground and excited states for the hydrogen molecular ion, helium, lithium and the hydrogen molecule. The calculations required increase at a modest rate with increasing numbers of particles.

06.2-03 FORBIDDEN BRAGG (222) REFLECTION IN DIAMOND STRUCTURE CRYSTALS. L.I.Kleschinsky Yu.A.Rosenberg, V.M.Kiselev, A.I.Kolosovsky, I.L.Feldman, Yu.M.Rotner, Phys. Dept., Institute of Transport's Engineers, Irkutsk 664028, U.S.S.R.

Absolute integrated intensities of (111), (333) and forbidden (222) reflections were measured on double-crystal spectrometer with CuK_α and MoK_α radiations in single crystals of natural and synthetical diamond, perfect silicon and germanium.

Description of antisymmetric charge density are given for all crystals and modifications of atomic centrosymmetric charge density as compared to free state are characterized quantitavely.

Perfection of diamond single crystals studied by Renninger effect as well as results obtained using different extinction corrections are discussed.

06.2-04 STRUCTURAL INVESTIGATION AND CHARGE DENSITY OF THIAMIN NITRATE. By A. TURANO, W. FUREY, J. PLETCHER, D. YANG AND M. SAX Biocrystallography Laboratory, VA Medical Center, Pittsburgh, Pa 15240 Department of Crystallography, University of Pittsburgh, Pittsburgh, Pa. 15260

Thiamin mononitrate is monoclinic, $P_{2_1/c}$, a=6.529(6), b=12.217(7), c=18.51(1)Å, β=97.9°(1), $^{Z=4}_{1}$. Data was collected on a CAD4 diffractometer at -75°C using MoKα radiation. The molecule was refined by full matrix least squares techniques to an R value of .048 using 2492 observed reflections. Charge density analysis using deformation maps and direct space integration over atomic volumes yielded individual atomic charges. Direct space integration was found to be less sensitive to thermal effects in deducing the charge, than reciprocal space techniques. Structural investigation and charge density studies on Vitamin B_1 have been conducted to gain information about the mechanism of action of this coenzyme on various biosynthetic pathways. Charge density studies of thiamin nitrate revealing the electronic structure should provide valuable insight about the chemical properties of the molecule.