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COMMENTS AND ADDENDA

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Low-Energy-Electron Diffraction from Al(100), Al(110), Al(111), and Cu(100)[†]

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The results of model calculations of the intensities of low-energy electrons, $20 \lesssim E \lesssim 200$ eV, scattered from Al(100), Al(110), Al(111), and Cu(111) and performed using a three-partial-wave inelastic-collision-model analysis, are presented. Comparison of a comparable matrix-inversion analysis with the second-order perturbation calculation of Tong and Rhodin indicates the accuracy of perturbation theory for strong potentials which cause predominantly forward scattering. Each member of a set of models which includes that of Tong and Rhodin describes well the scattered intensities from Al(100) near normal incidence. However, the models fail to describe adequately a more extensive set of data taken at larger angles of incidence and on the (110) and (111) faces. Comparisons between model calculations and absolute-intensity measurements for Cu(100) indicate that the model describes satisfactorily the nonspecular absolute intensities but not those of the specular beam for small values of the angle of incidence.

In a recent letter[1] Tong and Rhodin reported the results of a complete second-order perturbation-theory calculation of low-energy-electron diffraction (LEED) intensities from Al(100). Without using any arbitrarily adjustable parameters they achieved a satisfactory description of that portion of Joha's experimental data to which they compared their results.[2] Our examination of electron scattering from solids suggest that at least three aspects of Tong and Rhodin's study merit further consideration. First, in the case of aluminum Jona's data suggest the occurrence of significantly different "inner-potential" shifts on the three most densely packed faces [i.e., (111), (100), and (110)]. Therefore model predictions should be compared with data on a variety of faces rather than those taken solely on the (100) face. Second, the agreement between theory and experiment is usually much better for small angles of incidence ($\theta \lesssim 10°$) than for large ones. Consequently a comparison between the model predictions and experimental data for large angles of incidence also should prove illuminating. Finally, the absolute magnitudes of the experimental intensities are not known for aluminum, so the same model should be tested on other materials for which these quantities are available. Indeed, a striking aspect of Tong and Rhodin's analysis is their achievement of a better description of the experimental data than might have been anticipated considering the poorly understood nature of many features of the electron solid force law.[3–5] In the context of examining the validity of various simple models of this force law, we have analyzed a somewhat wider range of experimental data via a method which does not involve the use of perturbation theory. Because the question of the adequacy of such models is a central one in the theory of LEED,[3] it seems appropriate to compare some of the main features of our results with those of Tong and Rhodin with the objective of delineating more precisely the domain of validity of these models. We proceed by defining our version of the model calculation, comparing the results for Al(100) obtained using their potential to those predicted using an augmented-plane-wave (APW) potential evaluated by Snow,[6] comparing analogous results for the (110) and (111) faces of aluminum both to those predicted by the *s*-wave version of the inelastic-collision model[3, 7–10] and to Jona's data,[2] and finally investigating the validity of the model's prediction of absolute LEED intensity by presenting the results of an analysis of Andersson's data[11] on Cu(100) based on the use of Snow's APW potential for copper.[12]

The model on which our calculations are based is the finite-temperature inelastic-collision model of LEED as constructed by Duke and Laramore.[13,14] The matrix-inversion analysis[8] of this model is used in which the electron-ion core scattering is characterized by three partial-wave phase shifts δ_l, $l \lesssim 2$. The use of more phase shifts proves prohibitively expensive on our computer. We ruled out the use of perturbation theory[7] because in the cases in which its predictions were interesting (i.e., the intensity profiles were not kinematical), they deviated from the exact ones by factors in excess of 100% at some of the "secondary" structures in the intensity profile.[8] Our results for $l \lesssim 2$ are quite comparable to those of Tong and Rhodin, who used $1 \lesssim 3$. However, for small angles of incidence at higher energies ($E \gtrsim 100$ eV) on Al(100) they seem to be less satisfactory than some recently obtained by Marcus and Jepsen,[15] who used $l \lesssim 8$. For purposes of comparison with Tong and Rhodin's results, we constrain the phase shifts of the bulk and surface atoms to be identical, although our calculations for other cases suggest that such a constraint is a severe one (see also Refs. 4, 7, and 8). The phase shifts used in our model either are calculated from bulk APW

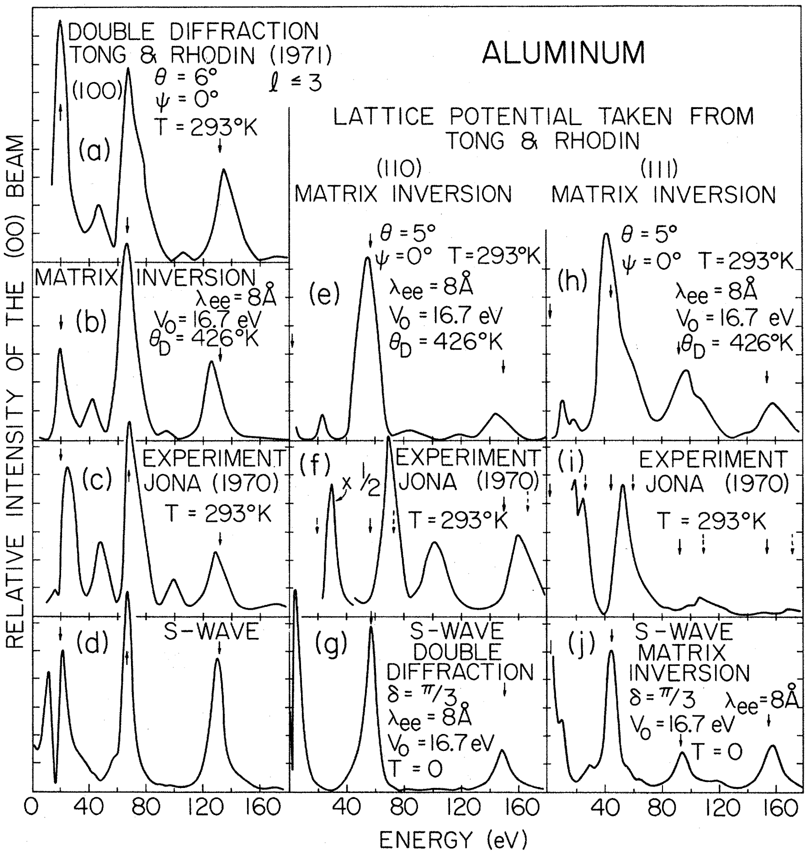


FIG. 1. Comparison between model predictions and experimental data for the specular beam of electrons scattered from Al(100), (110), and (111). The phase shifts for the potential were taken from Tong and Rhodin (Ref. 1) and the experimental data from Jona (Ref. 2). The angle of incidence θ and azimuthal angle ψ (defined in Ref. 2) are noted in the figure, as are the parameters used in the calculation. The lower left-hand panel was calculated using the double-diffraction approximation and the parameters indicated in the lower central panel. Solid arrows indicate the kinematical Bragg energies for an inner potential of $V_0 = 16.7$ eV which is equal to the sum of the Fermi energy and work function for Al (100). [It also is Snow's inter-ion-core APW potential (Ref. 6)]. Dashed arrows designate the kinematical Bragg energies for an inner potential $V_0 \equiv 0$.

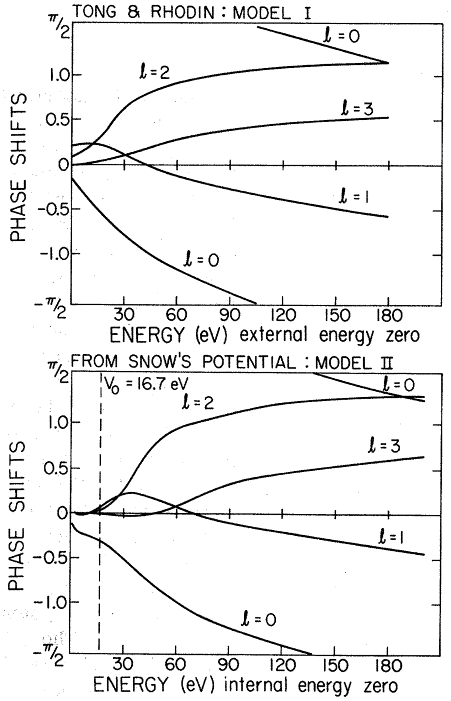


FIG. 2. Comparison of the phase shifts used by Tong and Rhodin (Ref. 1) (upper panel) with those obtained from the APW potential constructed by Snow (Ref. 6) (lower panel).

potentials,[6,12] or are taken directly from Fig. 1 in the paper by Tong and Rhodin.[1] Propagation of the electron between the "muffin-tin" potentials is described by the single-electron self-energy[7,8,14]

$$\Sigma(E) = -V_0 - (i\hbar^2/m\lambda_{ee})[(2m/\hbar^2)(V_0+E)]^{1/2}\,. \quad (1)$$

The quantity V_0 is required to be the constant potential between the ion cores used in the calculation of the APW potential.[6,12] The electron inelastic-collision mean free path is taken in the range $6 \leq \lambda_{ee} \leq 10$ Å as required by both theoretical and experimental estimates[16] in the energy range of interest ($25 \lesssim E \lesssim 200$ eV). Finally, we use the bulk Debye temperature to describe the effects of lattice vibrations in accordance with Eq. (61) of Laramore and Duke.[14] This model is known to be inadequate,[14] but it is that which is analyzed by other workers who examine temperature effects in dynamical models.[1,15,17] From the above consideration we see that the calculations reported herein also involve no "adjustable" parameters, although our model of $\Sigma(E)$ differs from that of Tong and Rhodin.[18]

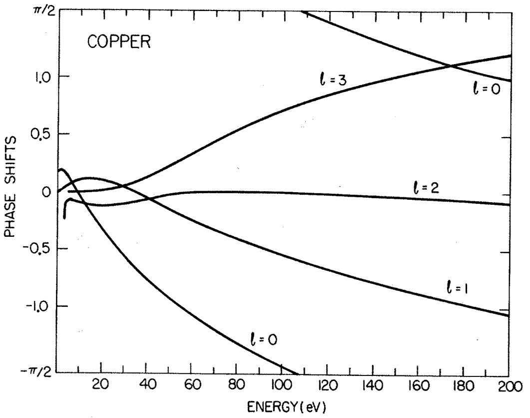
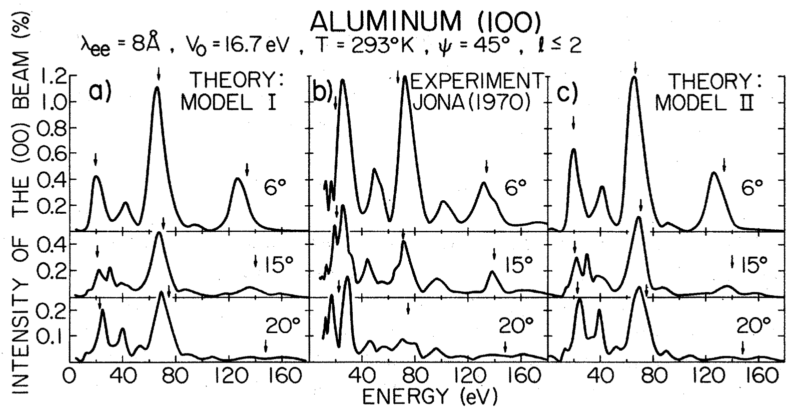


FIG. 4. Phase shifts resulting from Snow's (Ref. 12) APW potential for copper.

Turning to the first item in our results, we show in the left-hand panel of Fig. 1 the comparison between Tong and Rhodin's results,[1] our analyses based on their phase shifts but on the self-energy in Eq. (11), Jona's data,[2] and the s-wave inelastic-collision model.[8,10] The upper two panels illustrate well the distinctions to be expected between the second-order perturbation theory[1,7] and matrix-inversion[8] analyses: Peak heights of large peaks

FIG. 3. Comparison between model predictions and experimental data for the specular beam of electrons scattered from Al(100). The parameters describing the incident beam and model calculations are noted in the figure. Both "theory" calculations were performed using the matrix-inversion analysis described in the text and a Debye temperature of $\Theta_D = 426°$ for aluminum. Solid arrows indicate the kinematical Bragg energies for an inner potential of $V_0 = 16.7$ eV. The experimental data are those of Jona (Ref. 2).



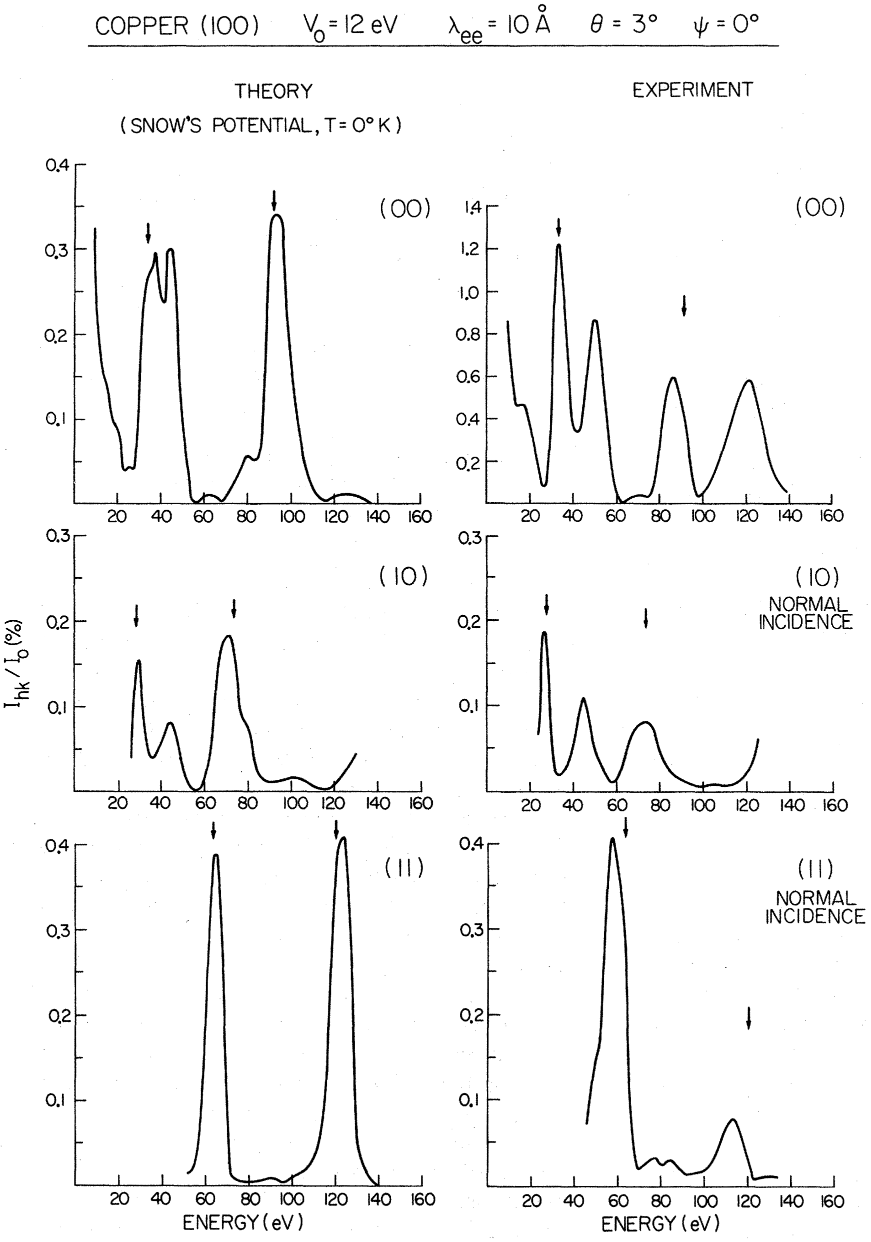


FIG. 5. Comparison between model predictions and experimental data for several beams of electrons scattered from Cu(100). The parameters describing the incident beam and model calculations are noted in the figure. Only the $l \leq 2$ phase shifts are used in the model calculation described in the text. The azimuthal angle ψ is measured relative to the simple-cubic (nonprimitive) surface unit cell (Ref. 11). Arrows designate the kinematical Bragg energies obtained using $V_0 = 12$ eV as required by Snow's interatomic muffin-tin potential (Ref. 19). The calculation is performed for $T = 0$ because Andersson's experimental intensities were measured using a spot photometer of unspecified angular aperture (Ref. 11). We find that the $T = 0$ calculation which assumes that the photometer measures thermal diffuse as well as elastic scattering (Ref. 4) describes the data better than a finite-temperature calculation which assumes an angular acceptance which is narrow relative to the thermal-diffuse "width" of the spot.

can vary by ± 50% (e.g., the one near 20 eV) and small peaks and dips can be interchanged (e.g., the structure between 90 and 110 eV). In terms of locating the major maxima in the intensity profile, the s-wave model works as well as either of the more sophisticated ones, although it is well known not to provide enough intensity in the "secondary" maxima.[8]

The difficulties incurred using the same "inner potential" V_0 on all three faces are evident in the figure. Although $V_0 = 16.7$ eV is satisfactory for the (100) face, the (110) face appears best described by $V_0 \cong 0$, whereas a satisfactory description of the data for the (111) face is obtained by using $V_0 \cong 7$ eV. These differences in apparent values of the inner potential lie outside the uncertainties in the dynamical parameters of the model,[3,4,16] and therefore they seem to require either a modified surface geometry or experimental error for their interpretation.[10]

Additional insight into the questions of the uniqueness of the potential and the description of intensity profiles at larger angles of incidence θ is achieved by presenting in Fig. 2 a comparison of the phase shifts from Tong and Rhodin's model with those resulting from Snow's APW potential. A comparison of the experimental intensity profiles with those predicted using these two sets of phase shifts in our model is shown in Fig. 3 for an azimuthal angle rotated by 45° from that used to construct Fig. 1. The agreement between the model predictions and the data again is excellent at $\theta = 6°$. However, it has degenerated badly by $\theta = 20°$, as is evident in the lower panels of the figure: a not unexpected result[3] in view of the degeneracies of various internal beams for $\theta \cong 0$; i.e., the intensity profiles for $\theta \gtrsim 10°$ are more sensitive to the ion-core scattering potentials than those for $\theta \cong 0$.

Arriving at our last topic, the prediction of absolute intensities by the model, we are forced to turn to another material, copper, because Andersson's data[11] on this substance are the only data available over a wide range of energies near normal incidence (i.e., in the range of parameters for which we expect the model predictions to be most reliable). The phase shifts obtained using Snow's APW potential[12,19] for Cu are shown in Fig. 4. In our model they lead to the intensity profiles which are compared to Andersson's data in Fig. 5. The value $\lambda_{ee} = 10$ Å was chosen at the upper limit of the physically reasonable range because Cu has only one s electron per ion core. In addition, the results are insensitive to λ_{ee} in the range of $\lambda_{ee} = 10 \pm 3$ Å. The agreement between the model predictions and experimental data appears quite satisfactory for the nonspecular beams both with regard to the visual appearance of the intensity profile and to its absolute magnitude. A reduction in the intensity of the higher-energy peaks would be obtained in a finite-temperature calculation which, however, is not directly comparable to the data in the absence of corrections for the angular acceptance of the spot photometer and multiphonon scattering.[4] The agreement between the model predictions and experimental data for the specular beam is poor with regard to both of the above figures of merit. The inclusion of higher partial waves $l \leq 8$ seems to improve the visual appearance of the profile (at the expense of an arbitrary inner-potential shift) but a discrepancy in the absolute magnitudes remains.[15] Upon inspection of Fig. 4 we would expect that for $E \gtrsim 50$ eV our model calculation would become increasingly inadequate as the energy is raised due to the rapid rise in the $l = 3$ phase shift between 40 and 100 eV. In fact, study of similar phase-shift calculations for Ag and W also led us to the conclusion that a satisfactory analysis of the electron-ion core scattering for $20 \lesssim E \lesssim 200$ eV required the use of at least five phase shifts, δ_l, $l \leq 4$, and consequently lies beyond our capacity to purchase the requisite computer time. The large values of the phase shifts which require the more extended range of δ_l also invalidate the application of second-order perturbation theory.[8] Consequently, using our present methods the necessary economy could be achieved only by failing to solve the Schrödinger equation with what we regard as the requisite accuracy (i.e., ±10% at all energies in the intensity profile).

In summary, the results reported herein indicate that although several simple microscopic models adequately describe electron scattering from Al(100) for $25 \lesssim E \lesssim 200$ eV near normal incidence, these same models fail to give a comparably satisfactory description of experimental data taken at larger angles of incidence ($\theta \gtrsim 10°$) or on the (110) and (111) faces of Al. Similar models give absolute intensities of the correct order of magnitude in Cu for electrons near normal incidence. However, the discrepancy between the model's capacity to describe the specular and nonspecular beams is not understood. Sufficient data to test the model predictions for Cu at larger angles of incidence and other crystal faces are not available. However, in all the cases discussed in this paper the comparison between the model calculations and the experimental data leads to discrepancies which may be attributed to uncertainties in the electron- solid force law, especially those concerning the positions of the ion cores in the surface layers of the solid.[3-5]

[†] Work was supported in part by the Advanced Research Projects Agency under Contract No. HC-15-67-C-0221.

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=7.5 eV in Eq. (1). More extensive unpublished calculations by these authors bear out our expectation that at larger angles of incidence, $\theta \geq 20°$, the agreement between the model calculations and experimental data has degenerated significantly. We are indebted to Dr. Jepsen, Dr. Marcus, and Dr. Jona for preprints of their results (which were submitted for publication after the submission of this manuscript).

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[18] In this context, we should note that the Jellium-model RPA calculations of $\lambda_{ee}(E)$ used by Tong and Rhodin are in disagreement with experimental data by factors of the order of 2 in all cases for which the model has been tested. We are indebted to Professor M. B. Webb for pointing this out to us in the case of Ag and to Dr. R. H. Ritchie in the case of Al.

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Calculation of the Physical Properties of Solids by the Extended Huckel Theory

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The philosophical and mathematical justifications for the use of the extended Huckel theory (EHT) in calculating the physical properties of solids are stated, difficulties with the use of EHT in its present form are pointed out, and methods for improving EHT calculations in solids are discussed.

The publication of the paper by Messmer and Watkins[1] on the calculation of the physical properties of diamond and of a nitrogen defect in diamond by the extended Huckel theory (EHT) illustrates once again the usefulness of this simple but elegant quantum-mechanical method of calculating the physical properties of molecules and crystals. EHT[2] is an approximation[3,4] of the rigorous Roothaan-Hartree-Fock[5] (RHF) linear combination of atomic orbitals molecular-orbital self-consistent-field (LCAO-MO-SCF) quantum-mechanical method. As such, there are some limitations in its use, particularly in crystals, most of which, happily, can be overcome. It is our purpose in this paper to state the philosophical and mathematical justifications for the use of EHT, to point out limitations in its use, particularly in crystals, and to suggest improvements to remove these limitations.

Philosophically, the use of EHT is justified because it may be applied at the present time to systems containing at least 200 atomic orbitals, i.e., 50 second- and third-period atoms, or more if hydrogen is one of the constituents, whereas rigorous SCF calculations are still limited to relatively few atoms. Thus many interesting systems are open to study by EHT but not by SCF methods.

The mathematical justification for the use of EHT in calculating the physical properties of molecules (and crystals, small regions of which may be regarded as large molecules) has been adequately described elsewhere.[3,4] Suffice it to say here that the use of EHT in calculating MO wave functions and MO energies is justified because the EHT equations to be solved have exactly the same form as the rigorous RHF[5] equations, i.e., the equations in both cases are

$$\sum_{\beta=1}^{n}(H_{\alpha\beta}-\epsilon_i S_{\alpha\beta})c_{i\beta}=0, \quad \alpha=1\ldots n.$$

In both methods α and β refer to AO's, i refers to MO's, $S_{\alpha\beta}$ are the overlap integrals between the n atomic orbitals χ_α and χ_β, ϵ_i are the MO energies, and $c_{i\beta}$ are the MO coefficients. There are n equations with n terms in each equation. The quantities solved for are ϵ_i and $c_{i\beta}$. In both methods $S_{\alpha\beta}$ are the same; however, in the RHF method $H_{\alpha\beta}$ are complicated functions of the MO coefficients and of two-, three-, and four-center integrals, and this fact necessitates solving the equations by iteration. On the other hand, in EHT the $H_{\alpha\alpha}$ terms are approximated by valence-orbital ionization energies and the $H_{\alpha\beta}$ terms are approximated by the Wolfsberg-Helmholz[6] expression $H_{\alpha\beta}=0.5KS_{\alpha\beta}\times(H_{\alpha\alpha}+H_{\beta\beta})$, or some similar expression. K is a constant usually taken to be between 1.0 and 2.0. If $H_{\alpha\alpha}$ and $H_{\beta\beta}$ have been judiciously chosen, then the EHT equations are quite similar to the last iteration of the RHF equations, and the resulting