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MASTER**EXTENDED HÜCKEL CALCULATION OF REPULSIVE INTERACTIONS IN NOBLE GASES*****Kristl B. Hathaway and James A. Krumhansl****Laboratory of Atomic and Solid State Physics
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Extended Hückel Calculation of Repulsive Interactions in Noble Gases*

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Abstract

Repulsive potential energies for all of the possible pairs of atoms of the noble gases helium, neon, and argon are calculated by the semiempirical extended Hückel molecular orbital method. The agreement of the calculated energies with other theoretical results and experimental data is significantly improved by computing overlaps using analytic approximations to the atomic Hartree-Fock atomic orbitals instead of the more commonly used Slater functions.

I. Introduction

Extended Hückel theory¹ is a simple semiempirical molecular orbital method capable of giving good approximations to the electronic structure of large molecules. We would like to extend this method to the calculation of atomic interaction energies in solids, with the goal of obtaining force constants for calculations of phonon spectra. This requires reasonably accurate potential energies for atomic displacements involving bond stretching, especially at the large atomic separations typical of solids. Extended Hückel method as it is usually applied does not give good potential energy curves for stretching displacements, although angular deformations are well represented.² In this and the following paper, we determine what improvements may be effected by some simple modifications of the standard methods.

There are many approximations inherent in the extended Hückel method which could contribute to the poor results for stretching displacements, and their relative importance probably varies with the type of atom under consideration. We focus here on the approximation of omitting the closed shell of electrons lying just below the valence electrons. For alkali atoms and other atoms with nearly empty valence shells, these closed shells contribute a large part of the repulsive potential energy. The calculations described in this paper show that extended Hückel theory can be applied to closed shell atoms with good results if approximations to the Hartree-Fock atomic wave functions are used in the computation of overlaps. We choose to test the method by calculating the interaction energy for pairs of atoms of helium, neon, and argon, both because these neutral, closed shell atoms avoid problems associated with charge dependence of the extended Hückel semiempirical parameters, and because they allow comparison with a large amount of experimental and theoretical data.

The next section discusses details in the application of extended Hückel theory to these systems. Results are presented in Section III, and the atomic wave functions are discussed in Section IV.

II. Method

The extended Hückel method has been described previously.¹ Calculations of molecular orbitals and energies are made for each pair of noble gas atoms at several atomic separations. The basis sets consist of all the electron states in the outermost occupied shell of each atom. Preliminary calculations indicate that inclusion of the 1s states in neon does not affect the results for the neon-neon interaction, so inner shells are neglected in all calculations reported here. Two sets of atomic orbital wave functions are used: The commonly used single exponential Slater type orbitals (STO) and linear combinations of STO's which better approximate the Hartree-Fock orbitals, especially in the overlap region. This second set of wave functions will be referred to as near Hartree-Fock orbitals (NHFO) and are obtained by various methods discussed below. Both sets of orbitals along with the semiempirical energy parameters are shown in Table 1. The repulsive interaction energy at each separation is obtained by subtracting the sum of occupied extended Hückel molecular orbital energies from the sum of one-electron energies for the isolated atoms.

III. Results

Calculated repulsive energies for the homogeneous systems He-He, Ne-Ne, and Ar-Ar are shown in Figures 1-3. The experimental comparisons are the repulsive terms from fits of experimental data to the Exp-6 potential, $\phi(r) = P_{\text{exp}}(-r/p) - \mu r^{-6}$ reported by Hill.³ The Self Consistent Field results are from calculations by Gilbert and Wahl⁴ using augmented atom optimized

basis sets. The Heitler-London calculation for neon is by Bleick and Mayer⁵ using analytic approximations to the Hartree-Fock functions; that for argon is by Kunimune⁶ using actual numerical Hartree-Fock results. The H-L type calculation shown for helium is an old calculation by Slater⁷ using an explicitly two-electron wave function.

In all cases, the STO results fall off too rapidly with separation, as would be expected. The NHFO results give better agreement with both the experimental and theoretical comparisons, especially for large separations. For helium, where the wave function is well represented by a single STO, there is little improvement in going to a two-term NHFO.

Hückel repulsive energies for the heterogeneous systems He-Ne, He-Ar, and Ne-Ar computed with NHFO's are compared with SCF results by Matcha and Nesbet⁸ in Figure 4, again showing reasonable agreement.

We emphasize that our primary purpose is to obtain a sufficiently good approximation for closed shell repulsions, to permit these repulsions to be included in extended Hückel calculations of force constants in solids. The present results indicate that the use of a closed shell basis set of NHFO wave functions in extended Hückel calculations yields repulsive energies in substantial agreement with both experiment and theory, without sacrificing the very attractive simplicity and speed of the extended Hückel method.

IV. Use of NHFO's

The variation of Hückel energy with separation depends directly on the variation of atomic orbital overlap through the Wolfsberg-Helmholtz expression for off-diagonal matrix elements, $H_{ij} = k S \frac{H_{ii} + H_{jj}}{2}$. The Hückel constant k can be adjusted to compensate for overall magnitude changes in overlaps associated with the use of different sets of atomic orbitals, but it cannot affect the separation dependence unless k is explicitly defined as a function of r .

In all of the cases studied here, the NHFO overlaps are computed to be greater than or equal to those for STO's over most of the range of separations, and fall off less rapidly with increasing r . The Hückel constant was accordingly decreased from 1.75 for calculations using STO's to 1.25 for NHFO's. Both sets of overlaps for argon are shown in Figure 5.

The type of NHFO's used in this calculation were suggested long ago by Slater⁹ who outlined a simple method to closely approximate a Hartree-Fock orbital by a fixed linear combination of a small number of STO's. Only the argon wave functions are computed exactly according to Slater's original prescription. The neon NHFO's are those of Brown¹⁰ employed by Eleick and Mayer in their calculation, and the helium function is Clementi's double-zeta function.¹¹ Other NHFO's are available from Roothan SCF results but these usually involve a larger number of STO's and require a significant increase in the time required to compute overlaps.

The importance of using wave functions with good overlap properties in extended Hückel calculations has been recognized before. Cusachs and Corrington¹² point out that single STO's with exponents optimized for energy cannot simultaneously give good approximations to the Hartree-Fock overlaps, and they recommend the use of overlap matched STO's. It is interesting to note that their preferred form for the off-diagonal energy matrix elements $H_{ij} = S(2 - |S|) \frac{H_{ii} + H_{jj}}{2}$, when used with STO's, has the effect of decreasing the fall-off of H_{ij} with atomic separation in much the same way as the use of NHFO's. Allen¹³ has noted a significant improvement in extended Hückel results for a wide range of molecules when self-consistent field atomic orbitals are used in the calculations.

It would be useful to test the validity of the Wolfsberg-Helmholtz approximation, $H_{ij} \propto S_{ij}$, for NHFO's. Much recent work attempting to justify this assumption¹⁴ is based on STO's, which, as shown in Figure 5, give widely varying overlaps.

V. Summary

We have shown by computation and comparison that physically plausible, generally straightforward, modification of the Slater orbitals in the extended Hückel method yields quantitative improvements in atomic interaction potentials. In another paper, we apply the method to small ionic molecules to compute vibrational parameters. In further work, we expect to examine both extended and cluster configurational energies in solids.

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References

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1. R. Hoffmann, J. Chem. Phys. 39, 1397 (1963),
R. Hoffmann and W. N. Lipscomb, ibid., 36, 2179 (1962); 37, 2872 (1962).
 2. A. B. Anderson and R. Hoffmann, J. Chem. Phys. 60, 4271 (1974).
 3. T. L. Hill, J. Chem. Phys. 16, 399 (1948).
 4. T. L. Gilbert and A. C. Wahl, J. Chem. Phys. 47, 3425 (1967).
 5. W. E. Bleick and J. E. Mayer, J. Chem. Phys. 2, 252 (1934).
 6. M. Kuninune, J. Chem. Phys. 18, 754 (1950).
 7. J. C. Slater, Phys. Rev. 32, 349 (1928).
 8. R. L. Matcha and R. K. Nesbet, Phys. Rev. 160, 72 (1967).
 9. J. C. Slater, Phys. Rev. 42, 33 (1932).
 10. F. W. Brown, Phys. Rev. 44, 214 (1933).
 11. E. Clementi, J. Chem. Phys. 40, 1944 (1964).
 12. L. C. Gusachs and J. H. Corrington in Sigma Molecular Orbital Theory,
O. Sinanoğlu and K. B. Wiberg, Eds. (Yale University Press, New Haven,
1970) p. 256.
 13. L. C. Allen, ibid., p. 227.
 14. For example see G. Blyholder and C. A. Coulson, Theor. Chim. Acta. 10,
316 (1968) and M. D. Newton, F. P. Boer, and W. N. Lipscomb, J. Amer.
Chem. Soc. 88, 2353 (1966).

Table I

**Atomic Wave Functions and Orbital Energy Parameters
Used in Extended Hückel Molecular Orbital Calculations**

			STO	NHFO		
Element	Orbital	Energy(ev) ^a	ζ^b	n	ζ	Coeff.
He	1s	24.5	1.70	1s	1.446	.8342
				1s	2.862	.1906
Ne	2s	48.5	2.85	1s	8.22	.2885
				2s	3.69	-.4867
				2s	2.15	-.6082
	2p	21.6	2.63	2p	3.80	.5507
				2p	1.69	.5365
Ar	3s	29.49	2.45	1s	14.72	.0865
				2s	5.44	-.3970
				3s	2.94	.5190
				3s	2.11	.6047
	3p	15.96	1.95	2p	6.52	.2848
				3p	2.71	-.6322
				3p	1.54	-.4680

^aFrom H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta (Berl.)* **3**, 458 (1965).

^bThe helium exponent is from Slater's rules for shielding constants (see, for example, J. C. Slater, *Quantum Theory of Matter*, (McGraw Hill, N.Y., 1951) p. 475); those for neon and argon are from Burn's rules (G. Burns, *J. Chem. Phys.* **41**, 1521 (1964)).

Figure Captions

- Figure 1: Computed interatomic potential V in electron volts vs. atomic separation R in Angstroms for two helium atoms. EXP, from experimental data, ref. 3; SCF, from self-consistent field calculations, ref. 4; HL, from Heitler-London type calculation, ref. 7; $\square$, extended Hückel calculation using STO's; $\square$, extended Hückel calculation using NHFO's.
- Figure 2: Computed interatomic potential V in electron volts vs. atomic separation R in Angstroms for two neon atoms. EXP, from experimental data, ref. 3; SCF, from self-consistent field calculations, ref. 4; HL, from Heitler-London type calculation, ref. 5; $\square$, extended Hückel calculation using STO's; $\square$, extended Hückel calculation using NHFO's.
- Figure 3: Computed interatomic potential V in electron volts vs. atomic separation R in Angstroms for two argon atoms. EXP, from experimental data, ref. 3; SCF, from self-consistent field calculations, ref. 4; HL, from Heitler-London type calculation, ref. 6; $\square$, extended Hückel calculation using STO's; $\square$, extended Hückel calculation using NHFO's.
- Figure 4: Computed interatomic potential V in electron volts vs. atomic separation R in Angstroms for heterogeneous noble gas diatomics. $\square$ extended Hückel calculation using NHFO's; solid lines from self-consistent field calculations, ref. 8.
- Figure 5: Computed overlaps between atomic orbitals of two argon atoms vs. atomic separation R in Angstroms. Solid line, NHFO's; dashed line, STO's.

He-He