EXTENSION OF A SIMPLIFIED CALCULATIONAL METHOD FOR SIGMA BONDED SYSTEMS TO HYDROGEN BONDING AMONG ELEMENTS OF THE SECOND AND THIRD ROWS

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CHAPTER I

INTRODUCTION

The *ab initio* solution of Schroedinger's equation for the ground state properties of molecular systems has progressed rapidly in recent years. With the appearance of digital computers with larger memory units and faster cycle times quantum chemistry is assuming the status of an accurate mathematical science. However, since the labor involved in a calculation rises very rapidly as the number of electrons considered increases, analytic solutions are still confined to relatively small chemical systems and are still approximate at best. It is therefore of interest to seek approximate solutions of the Schroedinger equation which yield a maximum of accuracy and information with a minimum of effort. The purpose of this study is to describe a calculational technique for obtaining approximate LCAO-MO solution of the Schroedinger equation for sigma bonded systems and to apply the method in calculations of some of the ground states of hydrogen bonded systems as a test of its effectiveness.

Review of Approximation Methods

Attention is restricted here to methods falling within the framework of LCAO-MO formulations. These methods use approximations which can be loosely characterized as the choice of which electrons of a system are explicitly treated and the techniques of evaluating the one and two electron interaction integrals which arise. The large majority of these treat only pi electron systems or are extended to all valence shell electrons of every atom in the molecular system. All the methods discussed here use empirical data to some extent in the evaluation of integrals.

Of the pi electron methods, the method formulated by Hückel (1-3) in which no two electron interactions are explicitly considered and the method formulated by Pariser and Parr (4,5) and extended by Pople (6) for the pi electron systems of organic molecules are very successful in view of their simplicity in correlating and predicting pi electron properties at experimental geometries. Some of the features of these two methods are present in many of the widely used all valence electron methods. Very characteristic is the application of zero differential overlap (ZDO) in varying degrees when evaluating overlap and two electron integrals.

The extended Hückel theory (EHT) introduced by Hoffmann (7) was an attempt to incorporate the sigma electronic systems of organic molecules into the calculations of molecular properties. Overlap integrals were explicitly calculated while two electron integrals were ignored. When applied to a variety of hydrocarbons, the method yielded good qualitative results in the prediction of preferred geometries of both planar and non-planar molecules.

The iterated extended Hückel theory (IEHT) formulated by Rein, et. al. (8) attempted to correct the omission of two electron repulsions in EHT by assuming a linear dependence of the ionization potential of an atom on the net atomic charge. Ionization potentials and dipole moments for sixteen molecules were reported and were judged to be in satisfactory agreement with experiment.

Three closely related methods were introduced by Pople and coworkers (9-13) in an attempt to reproduce minimal bases Hartree-Fock results by semiempirical means and were designed to apply to all molecular systems. The method of complete neglect of differential overlap (CNDO) applied the ZDO approximation to overlap and two electron integrals, the method of intermediate neglect of differential overlap (INDO) allowed one center exchange integrals into the calculational scheme and the most complicated of the three schemes, the method of neglect of diatomic differential overlap (NDDO) neglects only those two electron integrals for which the distribution of either electron is a product of atomic orbitals centered in different atoms.

Other all valence electron methods which have been proposed and applied have been the (modified INDO) MINDO method of Dewar et. al. (21,22), the EMZDO (exchange modified zero differential overlap) method of Dixon (22), and the method of Klopmann (14-16), all of which correspond roughly to the INDO method in terms of integral approximations, and the PNDO method of Dewar, et. al. (18-20) corresponding to a CNDO type of procedure.

In contrast to these pi electron and all valence electron methods, Pohl et. al. (23) developed a semiempirical method for sigma two electron systems in which no integral was neglected. It is the extension and application of this method termed the RDAO method by Mickish and Pohl (26) which will be of concern in this work. The RDAO method deviates from the trends of past formulations by treating only those electrons considered to be taking part in the bonding with no assumption of ZDO, i.e., every integral appears explicitly. When applied to the hydrogen halides (23,24), fair agreement with experiment was achieved for bond energies, equilibrium bond distances, dipole moments, and vibrational force constants using a closed shell wave function (23) with even better agreement being obtained with the use of a split shell wave function (24). The method was applied to the interhalogens by Pohl and Raff (25) and to hydrogen bonded systems involving N, O, and F by Mickish and Pohl (26).

Characteristics of Hydrogen Bonded Systems

The hydrogen bond (referred to hereafter as the H-bond and symbolized as X-H··Y) is a weak chemical association with an energy of formation of an order of magnitude or more smaller than the usual chemical bond but has considerable effects upon the properties of substances in which it is found. Examples of affected properties are dielectric constants, boiling and melting points, ferroelectric behavior, and infrared and Raman spectra (27). The importance of the H-bond in biologic systems is well illustrated by the fact that this is the chemical mechanism by this genetic information is stored in DNA (28).

For purposes of characterization, the operational definition of Pimentel and McClellan (27) will be used:

> "A H-bond exists between a functional group X-H and an atom or a group of atoms Y in the same or a different molecule when
>
> (a) there is evidence of bond formation,
> (b) there is evidence that this new bond linking X-H and Y specifically involves the hydrogen atom already bonded to X."

With this definition several quantities present themselves as amenable to calculation; the binding energy of the formation of the complex, the alteration in the equilibrium geometry of the X-H bond, the alteration in the potential energy surface of the proton upon formation of the H-bond, and changes in the vibrational spectra of the proton.

Previous Hydrogen Bond Calculations

The H-bond has been treated quantum mechanically using a variety of methods and approximations for a variety of specific systems. These treatments have ranged from purely empiric evaluations of the proton potential (29-31) to highly sophisticated *ab initio* calculations such as those undertaken by Clementi (32,33) and Clementi and Gayles (34) for the reaction

$$NH_3 + HCl \rightleftarrows NH_4Cl$$

and some perturbation calculations on a model system (35,36) and on $L_i\text{-}H\cdot\cdot L_i^+$ (37).

Studies using valence bond (VB) wavefunctions have been confined to four electron models for the H-bond and have dealt for the most part with the O-H••O system (38-43). A semi-empiric valence bond study was performed by Coulson and Danielsson (38) to estimate the contributions of various resonance structures in the O-H••O system, Tsumobura (39) used an analytic VB method to study the delocalization energy, and McKinney and Barrow (40) used a VB wave function assuming the electronic potentials to be square wells obtaining a double well potential for the motion of the proton. Hasegawa et. al., (41-43) performed a non-empirical VB calculation on the O-H••O system using the same approximations as an earlier MO calculation by Weissmann and Cohen (44) to study the proton potential, shifts in the O-H equilibrium distance and O-H vibrational frequencies, and the ionic defects in water and ice.

The bulk of quantum mechanical calculations on H-bonded systems have used the MO formulation to quantitatively examine such properties as binding energies, geometries, dipole moments, proton potentials, and infrared spectral shifts upon the formation of the H-bond in many systems. Paoloni (45) made a qualitative study of the O-H··O bond discussing the dependence of the energy of bond formation upon hybridization of the basis set orbitals. Qualitative examinations of polarization energies in H_2O, HF, H_2S, and HCl were performed by Fischer-Hjalmars and Grahn (46,47). Weissmann and Cohan (44) used a four electron model of the H bond in the water dimer with the other valence shell electrons considered as static charge distributions.

All valence electron *ab initio* calculations (32-33, 48-58) have been performed for ionic (strong) (48-49, 50, 53, 54) and uncharged (weak) (32-33, 50, 52, 55-58) systems for wave functions, equilibrium geometries, binding energies, and spectroscopic properties. The systems treated have generally been relatively small, e.g. $(H_2O)_2$ (49, 50, 56, 57) and $(HF_2)^-$ (48, 51).

Of greater significance to this study are the semi-empirical calculations that have appeared within the past ten years as these are the works most readily comparable to results reported here. Of particular interest are some of the CNDO/2 (59-61) calculations on dimer and mixed dimer systems. Hoyland and Kier (59) treated the preferred conformation, binding energies, and monomer separations obtaining good results for dimers of water, ammonia, ammonium ion and methyl-ammonium ion water systems, methanol, and hydrogen flouride. Less satisfactory results were obtained for formic acid and acetic acid while consideration of hydrogen cyanide produced complete failure. Kollman and Allen

(60) used the CNDO/2 method on dimers and polymers involving hydrogen flouride, water, and ammonia for selection of conformations of the dimers, binding energies, and vibrational force constants. More complicated NDDO calculations produced markedly worse results. Sabin (61) attempted to extend the CNDO/2 formalism to the hydrogen sulfide dimer obtaining a binding energy much larger than experiment and an S••S distance much too small. Sabin at the same time performed an *ab initio* calculation which gave much better predictions of both quantities. Other semiempirical calculations have been made on water by Rein, et. al., (62) using the IEHT method in which no dimer stability was found and Murthy and Rao (63) using the EHT and CNDO/2 methods to compute proton potential curves and binding energies.

The largest systems involving H bonds treated with semiempirical systems have been the Pariser-Parr-Pople calculations N-H••N and O-H••N H-bonds in the quanine-cytosine base pair in DNA by Harris and Rein (64-66) and the extension by Lunnel and Sperber (67) to the H-bonding in the adenine-thymine, adenine-cytosine, and quanine-sytosine base pairs. A model using the pi-electrons and the four electrons of each H-bond was assumed to study the electronic structures, potential energy surfaces of the protons, tunneling of the protons, and tautomeric equilibria.

Problem Definition

The RDAO calculations by Mickish and Pohl (26) on the O-H••O, N-H••N, F-H••F systems utilized a four electron model for the H-bond with an SCF-LCAO-MO wave function. Experimental dimer separations were assumed for the X••X distance and the potential energy of the proton was calculated around the X-H equilibrium point. From these curves good correlation with experimental results was obtained for binding energies, X-H separations with and without conditions of H-bonding, and vibrational force constants.

Because of the success of these calculations, the semiempirical SCF calculations will be here extended by calculating the binding energies as a function of X••X separation and extending attention also to the mixed systems X-H••Y with the inclusion of the third row elements P, S, and Cl. Potential curves for the proton motion will be calculated and from these binding energies as a function of X••Y separations, X-H equilibrium distances, and vibrational force constants will be derived and compared with experiment.

In addition to these computations, the problem will be reformulated by use of a split shell wave function to determine if there is any improvement in results. The split shell wave function, first utilized by Coulson and Fischer (68) in their work on the H_2 molecule, allow electrons with opposite spins to occupy different molecular orbitals if this is energetically preferred by the system. This allows the dissociation of the molecular system into neutral atoms whereas the closed shell forces a dissociation into ionic parts a large separations of the cores. Besides the work of Harris and Pohl (24) on the hydrogen halides the split shell function has been used by Harris, et. al., (69) in their work on the reaction potential surface of H_3.

A third and final part of the problem is to attempt an analytic RDAO approach to FH in which the valence shell electrons not participating in the bond are considered as static charge distributions after the manner of Weissmann and Cohan (44). If results are deemed favorable, the approach will be extended to an analytic four electron model of $(FH)_2$.

CHAPTER II

THE RDAO METHOD AND SEMI-EMPIRIC INTEGRAL APPROXIMATIONS

In this chapter the RDAO method will be described and the necessary equations developed for the application of the SCF closed shell and the split shell wavefunctions to the four electron, three center H-bonded system. In addition, the semiempiric approximations for the RDAO-1 calculations will be given.

LCAO-MO Variational Solution of the Schroedinger Equation

The non-relativistic quantum mechanical calculation of the ground state properties of a molecular system demands the solution of the time-independent Schroedinger equation

$$\hat{H}\Psi_o = \varepsilon_o\Psi_o \,. \qquad (1)$$

Ψ_o is a function of the 3N space and N spin coordinates of the N electrons and the hamiltonian operator $\hat{H}$ is the sum of one electron kinetic energy and nuclear attraction operators and the electron-electron repulsions,

$$\hat{H} = \sum_{i=1}^{N} \left[-\tfrac{1}{2}\nabla_i^{2} - \sum_{\gamma=1}^{M} \frac{Z_\gamma}{R_{i\gamma}}\right] + \sum_{i<j} \frac{1}{r_{ij}} \qquad (2)$$

where the electronic quantities are labeled by lower case latin indices and the nuclear quantities by greek indices. Equation (2) is written in the atomic system of units for which $h = m_e = |e| = 1$. Z_γ is the positive nuclear core-core charge in units of $|e|$. These units will be used throughout unless otherwise specified.

Equation (1) is actually an approximation to the full problem since the Born-Oppenheimer approximation has been applied in order to separate the solution of the electronic wavefunction from the nuclear wavefunction. The nuclear coordinates then appear in the wavefunction Ψ_o as parameters. The total energy of the system in this approximation is

$$E = \varepsilon_o + \sum_{\gamma<\delta} \frac{Z_\gamma Z_\delta}{R_{\gamma\delta}} \tag{3}$$

where $R_{\gamma\delta}$ is the separation between nucleu γ and δ.

The wavefunction Ψ_o is constrained to be finite and continuous in the 3N electron coordinate space and must also be antisymmetric under the interchange of any two electrons in order to conform to the permutational invariance of the hamiltonian operator and to satisfy the Pauli principle. These requirements can be satisfied by a wavefunction which is a linear sum of determinants of one electron functions

$$\Psi_o = \Sigma\, C_I D_I \tag{4}$$

where the coefficients $\{C_I\}$ are pure numbers and each D_I is a determinant of N linearly independent on electron spin orbitals, e.g.

$$D_I = \begin{vmatrix} \lambda_1(1) & \lambda_2(1) & \cdots & \lambda_N(1) \\ \lambda_1(2) & \lambda_2(2) & \cdots & \lambda_N(2) \\ \vdots & & & \vdots \\ \lambda_1(N) & \lambda_2(N) & \cdots & \lambda_N(N) \end{vmatrix} \tag{5}$$

where the electron coordinates have been indicated by the index of that particular electron. In principle, Ψ_o may be found exactly as an expansion in a complete set of these determinants but in practice is approximated by a finite sum of the determinants considered to make the most important contributions.

A molecular spin orbital λ_i is composed of a purely spacial function ψ_i multiplied by one of the spin functions α or β;

$$\lambda_i = \psi_i\alpha,\ M_s = +\frac{1}{2}$$

or

$$\lambda_i = \psi_i\beta,\ M_s = -\frac{1}{2} \tag{6}$$

The spacial molecular orbitals (MO's) are written as linear combinations of atomic orbitals (LCAO's)

$$\psi_i = \sum_{\mu=1} c_{i\mu}\, \chi_\mu \tag{7}$$

With this form for the wavefunction, equation (1) is solved by the application of the variational theorem. A trial wavefunction Ψ is chosen which contains a number of variable parameters. These parameters are varied until a minimum value for the electronic energy ε is found where ε is given by

$$\varepsilon = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}\ . \tag{8}$$

The variational theorem then says that this minimum value of ε forms an upper bound for ε_0.

The RDAO Method

The application of the *ab initio* Hartree-Fock LCAO-MO formulations to molecular systems is beset with the well known difficulties of the evaluation of multicentered integrals, number of integrals needed and the size of the matrices to be diagonalized in the solution of the secular equation. The all valence electron methods described in Chapter

I have dealt with the first two of these difficulties by semiempiric evaluation of the integrals involved and by application of the ZDO assumption to reduce the number of integrals but do nothing about the third complication.

The RDAO method reduces the problem by reducing the number of electrons explicitly considered to be forming the bond with just enough basic AO's to form the necessary MO's. Since the number of integrals involved varies approximately as n^4, the number of two electron integrals, where n is the number of basis AO's, a reduction in the number of basis AO's results in a much larger reduction in the number of integrals. It also reduces the size of the matrices in the eigenvector-eigenvalue problem.

The diatomic molecule FH provides an example of these reductions. In the RDAO treatment two basis AO's would be used, one centered on F and one, on H. This gives 2 x 2 matrices in the SCF secular equation with 2^4 two electron integrals to be considered. In an all-valence electron scheme there would be eight electrons in the problem with at least 4 basis AO's centered on F and one on the proton. There would then be 5 x 5 matrices in the SCF secular equation with 5^4 two electron integrals to be considered.

To reduce the number of electrons explicitly considered the hamiltonian and the wavefunction are required to implicitly reflect the interactions with the rest of the electronic system. Regarding these other electrons merely as reductions of the nuclear charge is obviously insufficient for then a single hamiltonian operator could be written for a large number of systems, e.g. the FH and H_2 molecules would have the same hamiltonian. An unrestricted variational solution would then give a single description for a great many molecular systems.

The RDAO wavefunction is constrained by choosing the AO's used to construct the MO's and then holding them fixed throughout the calculation, i.e. the set of coefficients $\{c_{i\mu}\}$ are the only parameters subjected to the variation. The AO's are chosen to reflect the atomic environment of the electron contributed to the bond, e.g. approximations to the Hartree-Fock AO's. This constraint on the basis AO's provides the name of this method, the method of Restricted Domains of Atomic Orbitals.

The electronic core potentials are the parts of the hamiltonian which contain the interactions of the bond electron with the remaining parts of the atom. In the semiempirical formulation of the method, the explicit specification of the core potentials can be avoided as shown in a later section of this chapter. The analytic formulation does not allow this simplification. In this study the remaining valence shell electrons will be assumed to be static charge distributions given by the occupation of appropriate valence shell AO's.

Another feature of the RDAO method is to provide for a variation of the shielding of the core charges with varying core-core separations in the calculation of core-core repulsion energies. This provides for the lessened shielding of the core charge under penetration of the surrounding charge cloud.

The general features of the RDAO method besides those possessed by any LCAO-MO method as described in the preceding section may be summarized as below.

1. Only bonding electrons are explicitly treated.
2. All integrals involving bonding electrons are explicitly

evaluated.

3. The AO's are chosen prior to the variation procedure and are then held fixed. The parameters varied are the coefficients of the AO's in the MO's.

4. The electronic core potentials reflect the interactions with the remaining electrons of the atom.

5. Core-core interactions may include shielded potential terms for small internuclear distances.

The Model For The Hydrogen Bond

A four electron model was used for the calculation of ground states properties of the hydrogen bonded systems X-H••Y where X and Y are highly electronegative atoms in the second and third rows of the periodic table. A linear geometry was assumed for the atomic core configuration with the line joining the three centers being taken as the Z-direction. One electron was assumed to be contributed by center X to the bond, one by the hydrogen atom, and two from a lone pair of electrons on center Y.

One AO was assigned to each of the centers X and Y and were constructed to be tetrahedral hybridizations of 2S and 2pz or 3S and 3pz orbitals of the form first proposed by Slater (70) and Zener (71). These orbitals have the form

$$\chi_{n\ell m} = N\, r^{n^{*}-1}\, e^{-r\zeta} Y_{\ell}^{m}(\nu,\psi) \qquad (9)$$

where N is the normalizing constant, n^{*} has the function of being the principal quantum number and Y_{1}^{m} is the spherical harmonic. n^{*} and ζ are evaluated according to the rules formulated by Slater. For the case here,

$$\begin{aligned} \chi_{200} &= \chi_{2S} = N_{2S} r e^{-\zeta r} \\ \chi_{300} &= \chi_{3S} = N_{3S} r^2 e^{-\zeta r} \\ \chi_{210} &= \chi_{2pz} = N_{2pz} r e^{-\zeta r} \cos \nu , \\ \chi_{310} &= \chi_{3pz} = N_{3pz} r^2 e^{-\zeta r} \cos \nu . \end{aligned} \tag{10}$$

The tetrahedrally hybridized orbitals used to construct the electronic wavefunction have the form (73)

$$\chi_{rte} = \frac{1}{2}(\chi_{ns} + \sqrt{3}\,\chi_{npz}) \tag{11}$$

The hydrogenic 1s AO was used to describe the hydrogen center in the SCF calculations with the $2p_z$ function being added to the basis set for the split shell computations. This last function was added in order to be able to construct the four linearly independent MO's required by the split shell formulation.

The schematic of core configurations and AO's is shown in Figure 1 along with the indexing of AO's and internuclear distances used. Center X will always be indexed as 1, H as 2, and Y as 3.

The hamiltonian operator for this system is

$$\hat{H} = \sum_{i=1}^{4}[-\tfrac{1}{2}\nabla_i^2 + V_1(i) + V_2(i) + V_3(i)] + \sum_{i<j}^{4} \frac{1}{r_{ij}} \tag{12}$$

where $V_1(i)$, $V_2(i)$ and $V_3(i)$ are the potential energy operators of electron i with repsect to center X, the proton, and center Y. The one electron hamiltonian is therefore

$$h(i) = -\tfrac{1}{2}\nabla_i^2 + V_1(i) + V_2(i) + V_3(i) \tag{13}$$

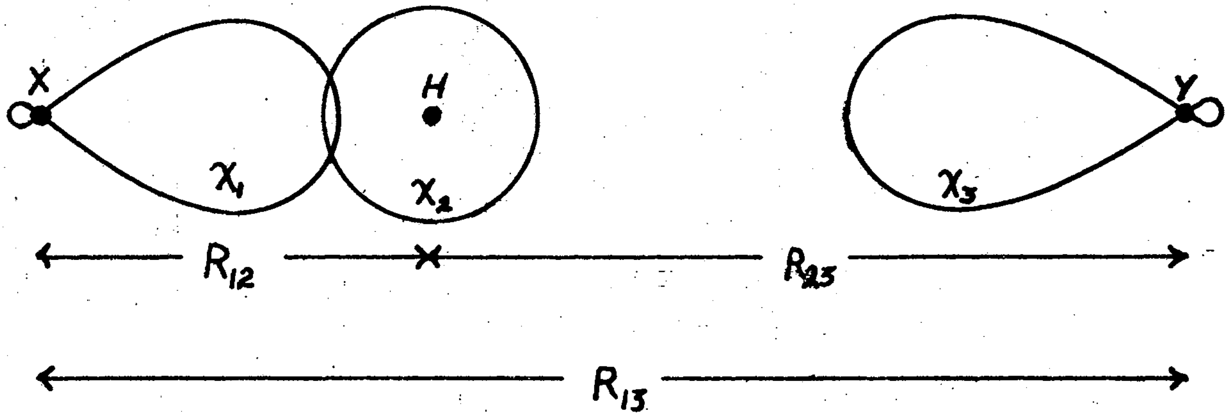

Figure 1. Schematic of Three Center H-Bond

where

$$\hat{H} = \sum_{i=1}^{4} h(i) + \sum_{i<j}^{4} \frac{1}{r_{ij}} \qquad (14)$$

The total energy of the X-H··Y system is

$$E = \varepsilon + V_{12} + V_{13} + V_{23} \qquad (15)$$

where ε is the electronic energy found in the variational calculation and $V_{\gamma\delta}$ is the repulsion energy of cores γ and δ. For a fixed value of $R_{X\cdot\cdot Y}$ this energy E becomes the potential energy for the motion of the proton and the potential energy well for the proton is obtained by plotting the values of E at various values of R_{X-H}. The equilibrium value if R_{X-H} is then obtained by locating the minimum in the potential well.

The maximum binding energy for the X-H··Y complex is obtained as a function of $R_{X\cdot\cdot Y}$ by calculation of

$$\Delta E = E - E_o \qquad (16)$$

at the equilibrium values of R_{X-H} where E_o is the equilibrium total energy for an infinite value of $R_{X\cdot\cdot Y}$. If binding is predicted to occur then a plot of ΔE against $R_{X\cdot\cdot Y}$ will give another well. The equilibrium value of $R_{X\cdot\cdot Y}$ will occur at the minimum of the well and the maximum binding energy of the complex will be given by the well depth.

Since the potential energy for the linear motion of the proton is known, the force constants for the stretching vibration of the proton can be obtained by assuming a parabolic approximation to the proton potential well around the equilibrium point,

$$V = \tfrac{1}{2}k_{X-H\cdot\cdot Y}\,(R_{X-H} - R^{o}_{X-H})^2 \qquad (17)$$

where R^{o}_{X-H} is the equilibrium value of R_{X-H} for a constant $R_{X\cdot\cdot Y}$. This force constant is related to the proton vibrational frequency at vanishingly small amplitudes by

$$k = 5.8883 \times 10^{-2} \mu \, \omega_e^{2} \tag{18}$$

where μ is the reduced mass of the X-H system, k is in units of dyne/cm and ω_e has units of cm^{-1} (94). The proton frequency at finite amplitudes decreases slowly from the value given by Equation (18) as anharmonic potential energy terms become more important. The experimental anharmonic frequency is obtained as the frequency of the IR radiation emitted or absorbed when the vibrator undergoes a transition from one energy state to another consecutive energy states.

In the case of the X-H··Y complex, there are three normal modes of vibration. One mode is the linear translation of the system as a whole, one is a slow vibration of the outer, massive X and Y centers with the proton vibrating in phase with X, and the third one is a faster vibration in which most of the energy of motion is associated with the proton. It is this third mode that corresponds with the force constant in Equations (17) and (18), the energy in Equation (15), and the IR spectra of the proton and which will be of interest in this study.

Self Consistent Field Formulation

In the SCF formulation the wave function in Equation (4) is a single determinant of molecular spin orbitals. Each MO occurs twice in the determinant, once with spin α and once with spin β, i.e., each MO is occupied by two electrons. This defines the "closed shell" configuration. The trial wave function is therefore

$$\Psi = \mathcal{A}\{\psi_1(1)\ \alpha(1)\ \psi_1(2)\ \beta(2)\ \psi_2(3)\ \alpha(3)\ \psi_2(4)\ \beta(4)\} \qquad (19)$$

where A is the antisymmetrizer and is given by

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \qquad (20)$$

where P is a permutation operator acting on all space and spin coordinates of all N electrons described by the function Ψ. Unless otherwise stated when a product of (spin) orbitals is written as in Equation (19) with electron indices missing, it is to be taken to mean that electron 1 occupies the first (spin) orbital, electron 2 the second (spin) orbital, etc. It will also be taken to mean that when the spacial orbitals and spin functions are grouped separately the spin function written first will belong with the first spacial orbital, etc., Ψ, for example, then is denoted alternatively as

$$\begin{aligned} \Psi &= \mathcal{A}\{\psi_1\alpha\psi_1\beta\psi_2\alpha\psi_2\beta\} \\ &= \mathcal{A}\{\psi_1\psi_1\psi_2\psi_2\alpha\beta\alpha\beta\} \end{aligned} \qquad (21)$$

The two one-electron MO's are written as linear combinations of the three AO's

$$\psi_1 = \sum_{\mu=1}^{3} c_{1\mu}\ \chi_\mu$$

and (22)

$$\psi_2 = \sum_{\mu=1}^{3} c_{2\mu}\ \chi_\mu$$

with the set of coefficients $\{c_{i\mu}\}$ being the parameters varied to find the lowest energy.

The variational problem is solved self-consistently using the procedure of Roothaan (73). An initial set of coefficients $\{c_{i\mu}\}$ is chosen and used to calculate the Hartree-Fock hamiltonian matrix $\mathfrak{f}$ whose elements are given by

$$f_{\mu\nu} = h_{\mu\nu} + \sum_{\sigma,\rho} P_{\sigma\rho} \left[(\mu\nu|\sigma\rho) - \tfrac{1}{2}(\mu\rho|\sigma\nu) \right] \tag{23}$$

where

$$h_{\mu\nu} = \int_{\substack{\text{All}\\\text{Space}}} \chi_{\mu}^{*}(i)\ h(i)\ \chi_{\nu}(i)\ d\tau_{i} \tag{24}$$

$$(\mu\nu|\sigma\rho) = \iint \frac{\chi_{\mu}^{*}(i)\ \chi_{\sigma}^{*}(j)\ \chi_{\nu}(i)\ \chi_{\rho}(j)}{r_{ij}}\ d\tau_{i} d\tau_{j} \tag{25}$$

and

$$P_{\sigma\rho} = 2 \sum_{i=1}^{2} c_{i\sigma}\ c_{i\rho}\ . \tag{26}$$

The integrals in Equations (24) and (25) are carried out over all space and the summation in Equation (26) is over the occupied MO's only.

The Hartree-Fock equation

$$(\mathfrak{f} - \mathfrak{E}\,\mathfrak{S})\mathfrak{C} = 0 \tag{27}$$

is then solved for a new set of coefficients where $\mathfrak{C}$ is the matrix of coefficients, $\mathfrak{E}$ is the matrix of the orbital energies of the MO's and is diagonal, and $\mathfrak{S}$ is the AO overlap matrix defined by

$$S_{\mu\nu} = \int \chi_{\mu}^{*}(i)\ \chi_{\nu}(i)\ d\tau_{i} \tag{28}$$

The new set of coefficients is used to make a better guess for the wavefunction, a new $\mathcal{F}$ computed, etc. This iterative procedure is repeated until the initial wavefunction at the start of a cycle converges to the wavefunction obtained at the end of the cycle within the desired limits. The electronic energy ε is then calculated to be

$$\varepsilon = \tfrac{1}{2} \sum_{\mu,\nu} P_{\mu\nu} \left[h_{\mu\nu} + f_{\mu\nu}\right] \tag{29}$$

Split Shell Formulation

The split shell wavefunction is constructed to have the same symmetries as the closed shell function but to also allow each electron to occupy a different MO if this is energetically preferable. L_z, the z component of the total orbital angular momentum, is zero since the four MO's are constructed of AO's which have a z component of zero. Now, however, a single determinent such as in Equation (19) is no longer an eigenfunction of the square of the total spin when all four MO's are allowed to be linearly independent. In fact, the closed shell function is shown below to be a special case of the split shell function.

The one-electron orbitals are again constructed as LCAO's

$$\psi_i = \sum_{i=1}^{4} c_{i\mu}\, \chi_\mu, \quad i = 1,2,3,4\ . \tag{30}$$

The wave function is then

$$\Psi = \mathcal{A}\{\psi_1\psi_2\psi_3\psi_4 \textcircled{H}\} \tag{31}$$

where $\textcircled{H}$ is the spin function constructed such that its eigenvalues for $\vec{S}^2$ and S_z are zero. This spin function is constructed with the use of Löwdin's projection operator method (74) and is shown in the Appendix to be

$$\textcircled{H} = d_1\textcircled{H}_1 + d_2\textcircled{H}_2 \tag{32}$$

where $\textcircled{H}_1$ and $\textcircled{H}_2$ are two linearly independent spin functions for which the eigenvalues of $\vec{S}^2$ and S_z are 0. d_1 and d_2 are numerical coefficients which form part of the set of parameters varied to find the lowest energy for the system. $\textcircled{H}_1$ and $\textcircled{H}_2$ are shown in the Appendix to be

$$\begin{aligned} \textcircled{H}_1 &= \frac{1}{3}(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha) - \frac{1}{6}(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta) \\ \textcircled{H}_2 &= \frac{1}{3}(\alpha\beta\alpha\beta + \beta\alpha\beta\alpha) - \frac{1}{6}(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta) \end{aligned} \tag{33}$$

Substituting Equations (32) into (31) gives

$$\Psi = \mathcal{A}\{\psi_1\psi_2\psi_3\psi_4 \, [d_1\textcircled{H}_1 + d_2\textcircled{H}_2] \tag{34}$$

where $\textcircled{H}_1$ and $\textcircled{H}_2$ are given by (33). From (33) and (34) it is easily seen that under any of the three conditions $\phi_1 = \phi_2$ and $\phi_3 = \phi_4$ or $\phi_1 = \phi_3$ and $\phi_2 = \phi_4$ or $\phi_1 = \phi_4$ and $\phi_2 = \phi_3$, reduces to a single determinant of the form (23).

Since the anti-symmetrizer is a linear operator the wave function ψ is a sum of determinants of molecular spin orbitals and the variational problem cannot be solved with a self-consistent field method. The wave function (34) was therefore converted to the equivalent valence bond (VB) function. The beginning point of the transformation is to use (30) to write the product of MO's as

$$\psi_1\psi_2\psi_3\psi_4 = \sum_{\mu,\nu,\sigma,\rho}^{4} c_{1\mu}c_{2\nu}c_{3\sigma}c_{4\rho}\, \chi_\mu\chi_\nu\chi_\sigma\chi_\rho \tag{35}$$

and substituting this expression into the right hand side of (34) to obtain

$$\Psi = \sum_{r=1}^{2} \sum_{\mu,\nu,\sigma,\rho}^{4} d_r c_{1\mu} c_{2\nu} c_{3\sigma} c_{4\rho} \mathcal{A}\{\chi_\mu \chi_\nu \chi_\sigma \chi_\rho \textcircled{H}_r\} \tag{36}$$

This wave function has now been written as a linear sum of determinants of atomic spin orbitals. (36) is rewritten as

$$\Psi = \sum_{\gamma=1}^{\Gamma} b_\gamma \Psi_\gamma \tag{37}$$

where the $\{b_\gamma\}$ are the variational parameters and are functions of the sets $\{c_{1\mu}\}$ and $\{d_r\}$ and Γ is the total number of independent valence bond functions.

To complete the transformation the specific functions Ψ_γ and the transformation between the sets of coefficients must be determined. From Equations (34) and (35) it is seen that the transformations between the sets of coefficients are of fifth order and as such would be extremely difficult to solve. Since one-electron properties are not of interest here the transformations will not be solved. The set of VB functions $\{\psi_\gamma\}$ are deduced by arguments below.

A change of notation will be performed to one which will be more convenient to work with both algebraically and in writing the later computer program. A determinant of AO spin orbitals will be written as $(\mu\bar{\nu}\sigma\bar{\rho})$ where AO is indicated by its index and the spin function belonging to the AO by a bar over the index if $m_s = -1/2$. With this notation, for example,

$$\mathcal{A}\{\chi_\mu \chi_\nu \chi_\sigma \chi_\rho \alpha\alpha\beta\beta\} = (\mu\nu\bar{\sigma}\bar{\rho}) \tag{38}$$

Further, the appropriate permutation will be applied to each determinant such that the spin appearing in the second and fourth columns of the determinant will be β. The determinant $(\mu\nu\bar{\sigma}\bar{\rho})$ is then written as $-(\mu\bar{\sigma}\nu\bar{\rho})$. Using (33), the two general valence bond functions in (37) are then

$$\begin{aligned}
\psi^{1}_{\mu\nu\sigma\rho} &= \mathcal{A}\{\chi_\mu\chi_\nu\chi_\sigma\chi_\rho \textcircled{H}_1\} = -\tfrac{1}{3}[(\mu\bar{\sigma}\nu\bar{\rho}) + (\nu\bar{\mu}\rho\bar{\sigma})] + \tfrac{1}{6}[(\mu\bar{\sigma}\nu\bar{\rho}) + (\sigma\bar{\mu}\rho\bar{\nu}) \\
&\qquad + (\mu\bar{\nu}\rho\bar{\sigma}) + (\bar{\nu}\mu\bar{\sigma}\rho)] \\
\psi^{2}_{\mu\nu\sigma\rho} &= \mathcal{A}\{\chi_\mu\chi_\nu\chi_\sigma\chi_\rho \textcircled{H}_2\} = -\tfrac{1}{3}[(\mu\bar{\nu}\sigma\bar{\rho}) + (\sigma\bar{\mu}\rho\bar{\nu})] - \tfrac{1}{6}[(\mu\bar{\nu}\sigma\bar{\rho}) + (\nu\bar{\mu}\rho\bar{\sigma}) \\
&\qquad - (\mu\bar{\nu}\rho\bar{\sigma}) - (\nu\bar{\mu}\sigma\bar{\rho})]
\end{aligned} \tag{39}$$

It is clear that no AO can appear more than twice in a single determinant since the value of the determinant would then be zero, i.e., two columns would be identical. Further, if an AO does appear twice the associated spins must be antiparallel. The only determinants which appear then, are of the types $(\mu\bar{\mu}\sigma\bar{\sigma})$, $(\mu\bar{\mu}\sigma\bar{\rho})$, or $(\mu\bar{\nu}\sigma\bar{\rho})$ or any permutations of these where the indices are assumed to all be different.

For the case where there are only two unique AO's in the VB function, substitution into (34) gives

$$\begin{aligned}
\psi^{1}_{\mu\nu\sigma\rho} &= \begin{cases} (\mu\bar{\mu}\sigma\bar{\sigma}) & \text{for } \nu=\mu,\ \rho=\sigma \\ 0 & \text{Otherwise} \end{cases} \\
\psi^{2}_{\mu\nu\sigma\rho} &= \begin{cases} (\mu\bar{\mu}\sigma\bar{\sigma}) & \text{for } \rho=\mu,\ \nu=\sigma \\ 0 & \text{Otherwise} \end{cases}
\end{aligned} \tag{40}$$

so that the VB function in this case has the form $(\mu\bar{\mu}\sigma\bar{\sigma})$. Similarly for the VB functions which contain three different AO's, (39) reduce to VB functions of the form

$$\psi^{1,2}_{\mu\mu\sigma\rho} = \tfrac{1}{2}[(\mu\bar{\mu}\sigma\bar{\rho}) + (\mu\bar{\mu}\rho\bar{\sigma})] \tag{41}$$

or zero. Equations (39) cannot be simplified further when four distinct AO's appear.

The number of VB functions can be determined with the following simple combinatorial arguments. There are four independent AO's from which 12 VB function of the form $(\mu\bar{\mu}\nu\bar{\nu})$ can be made since there are 4 ways of choosing the first AO and then 3 ways of choosing the second. Only six of these determinants are unique since $(\mu\bar{\mu}\nu\bar{\nu})$ is the same as $(\nu\bar{\nu}\mu\bar{\mu})$. Likewise, there are 4 x 3 x 2 or 24 determinantal functions with 3 distinct AO's but only 12 unique functions of the type $\frac{1}{2}[(\mu\bar{\mu}\sigma\bar{\rho}) + (\mu\bar{\mu}\rho\bar{\sigma})]$. Again there are 24 determinants which can be made from 4 different AO's but only 12 functions of the type $[(\mu\bar{\nu}\sigma\bar{\rho}) + (\nu\bar{\mu}\rho\bar{\sigma})]$. There will only be three unique functions of this type since

$$[(\mu\bar{\nu}\sigma\bar{\rho}) + (\nu\bar{\mu}\rho\bar{\sigma})] = [(\sigma\bar{\rho}\mu\bar{\nu}) + (\rho\bar{\sigma}\nu\bar{\mu})]$$
$$= -[(\mu\bar{\rho}\sigma\bar{\nu}) + (\rho\bar{\mu}\nu\bar{\sigma})] = -[(\sigma\bar{\nu}\mu\bar{\rho}) + (\nu\bar{\sigma}\rho\bar{\mu})]$$

With these three functions only two linearly independent VB functions as (39) can be constructed. There are, then, 20 VB functions in the basis set. There are listed in Table I.

Using the wave function developed above, the eigenvector-eigenvalue equation to be solved is

$$(\mathbf{H}-\mathcal{E}\mathcal{S})\mathbf{b}=\mathbf{0} \tag{42}$$

where

$$S_{\gamma\delta} = \langle\psi_\gamma|\psi_\delta\rangle$$

and

$$H_{\gamma\delta} = \langle\psi_\gamma|\hat{H}|\psi_\delta\rangle \tag{43}$$

TABLE I

Z_α^{eff} SPLIT SHELL BASIS FUNCTIONS

$\psi_1 = (1\bar{1}2\bar{2})$

$\psi_2 = \frac{1}{2}[(1\bar{1}2\bar{3}) + (1\bar{1}3\bar{2})]$

$\psi_3 = \frac{1}{2}[(1\bar{1}2\bar{4}) + (1\bar{1}4\bar{2})]$

$\psi_4 = (1\bar{1}3\bar{3})$

$\psi_5 = \frac{1}{2}[(1\bar{1}3\bar{4}) + (1\bar{1}4\bar{3})]$

$\psi_6 = (1\bar{1}4\bar{4})$

$\psi_7 = \frac{1}{2}[(2\bar{2}1\bar{3}) + (2\bar{2}3\bar{1})]$

$\psi_8 = \frac{1}{2}[(2\bar{2}1\bar{4}) + (2\bar{2}4\bar{1})]$

$\psi_9 = (2\bar{2}3\bar{3})$

$\psi_{10} = \frac{1}{2}[(2\bar{2}3\bar{4}) + (2\bar{2}4\bar{3})]$

$\psi_{11} = (2\bar{2}4\bar{4})$

$\psi_{12} = \frac{1}{2}[(3\bar{3}1\bar{2}) + (3\bar{3}2\bar{1})]$

$\psi_{13} = \frac{1}{2}[(3\bar{3}1\bar{4}) + (3\bar{3}4\bar{1})]$

$\psi_{14} = \frac{1}{2}[(3\bar{3}2\bar{4}) + (3\bar{3}4\bar{2})]$

$\psi_{15} = (3\bar{3}4\bar{4})$

$\psi_{16} = \frac{1}{2}[(4\bar{4}1\bar{2}) + (4\bar{4}2\bar{1})]$

$\psi_{17} = \frac{1}{2}[(4\bar{4}1\bar{3}) + (4\bar{4}3\bar{1})]$

$\psi_{18} = \frac{1}{2}[(4\bar{4}2\bar{3}) + (4\bar{4}3\bar{2})]$

$\psi_{19} - \frac{1}{3}[(1\bar{3}2\bar{4}) + (3\bar{1}4\bar{2})] - \frac{1}{6}[(1\bar{2}3\bar{4}) + (2\bar{1}4\bar{3}) - (1\bar{2}4\bar{3}) - (2\bar{1}3\bar{4})]$

$\psi_{20} = \frac{1}{3}[(1\bar{2}3\bar{4}) + (2\bar{1}3\bar{4})] + \frac{1}{6}[(1\bar{3}2\bar{4}) + (3\bar{1}4\bar{2}) + (1\bar{2}4\bar{3}) + (2\bar{1}3\bar{4})]$

where each integration is over the whole space of the electron and H is the hamiltonian operator defined by (12). The lowest eigenvalue of this secular equation is then the ground state electronic energy.

To evaluate (42) and (43) it is necessary to evaluate the overlap and hamiltonian operator integrals between two determinants of the form $(\mu\bar{\nu}\sigma\bar{\rho})$. Elements of $\mathcal{S}$ and $\mathbf{H}$ will then be appropriate sums of these terms.

For the overlap between two general determinants,

$$\begin{aligned} <(\mu\bar{\nu}\sigma\bar{\rho})|(\varepsilon\bar{\eta}\chi\bar{\lambda})> &= <\mathcal{A}\{\mu\bar{\nu}\sigma\bar{\rho}\}|\mathcal{A}\{\varepsilon\bar{\eta}\chi\bar{\lambda}\}> \\ &= <\mu\bar{\nu}\sigma\bar{\rho}|\sqrt{4!}\,\mathcal{A}\{\varepsilon\bar{\eta}\chi\bar{\lambda}\}> \end{aligned} \tag{44}$$

since the antisymmetrizer has the property that $\mathcal{A}^{+}\mathcal{A} = \sqrt{N!}\,\mathcal{A}$. Using (20) and integrating over the spins

$$\begin{aligned} <(\mu\bar{\nu}\sigma\bar{\rho})|(\varepsilon\bar{\eta}\chi\bar{\lambda})> &= <\chi_\mu\chi_\nu\chi_\sigma\chi_\rho|\chi_\varepsilon\chi_\eta\chi_\chi\chi_\lambda - \chi_\varepsilon\chi_\lambda\chi_\chi\chi_\eta \\ &\quad - \chi_\chi\chi_\eta\chi_\varepsilon\chi_\lambda + \chi_\chi\chi_\lambda\chi_\varepsilon\chi_\eta> \\ &= s_{\mu\varepsilon}s_{\nu\eta}s_{\sigma\chi}s_{\rho\lambda} - s_{\mu\varepsilon}s_{\nu\lambda}s_{\sigma\chi}s_{\rho\eta} \\ &\quad - s_{\mu\chi}s_{\nu\eta}s_{\sigma\varepsilon}s_{\rho\lambda} + s_{\mu\chi}s_{\nu\lambda}s_{\sigma\varepsilon}s_{\rho\eta} \end{aligned} \tag{45}$$

where $s_{\mu\varepsilon}$ is the overlap between χ_μ and χ_ε, etc.

In a completely similar manner as above the matrix element of the hamiltonian operator between two determinants becomes

$$\begin{aligned} <(\mu\bar{\nu}\sigma\bar{\rho})|\hat{H}|(\varepsilon\bar{\eta}\chi\bar{\lambda})> &= <\chi_\mu\chi_\nu\chi_\sigma\chi_\rho|\hat{H}|\chi_\varepsilon\chi_\eta\chi_\chi\chi_\lambda - \chi_\varepsilon\chi_\lambda\chi_\chi\chi_\eta \\ &\quad - \chi_\chi\chi_\eta\chi_\varepsilon\chi_\lambda + \chi_\chi\chi_\lambda\chi_\varepsilon\chi_\eta> \end{aligned} \tag{46}$$

The hamiltonian is now written as the sum of two operators

$$\hat{H} = \hat{H}^{o} + \hat{H}'$$

where

$$\hat{H}^o = \sum_{i=1}^{4} h(i) \tag{47}$$

and

$$\hat{H}' = \sum_{i<j}^{4} \frac{1}{r_{ij}} \tag{48}$$

A single term in (46), e.g., $<\chi_\mu\chi_\nu\chi_\sigma\chi_\rho|\hat{H}|\chi_\varepsilon\chi_\eta\chi_\chi\chi_\lambda>$ then becomes

$$<\chi_\mu\chi_\nu\chi_\sigma\chi_\rho|\hat{H}^o|\chi_\varepsilon\chi_\eta\chi_\chi\chi_\lambda> + <\chi_\mu\chi_\nu\chi_\sigma\chi_\rho|\hat{H}'|\chi_\varepsilon\chi_\eta\chi_\chi\chi_\lambda> . \tag{49}$$

Substituting (47) into the first term of the last expression,

$$<\chi_\mu(1)\chi_\nu(2)\chi_\sigma(3)\chi_\rho(4)|\sum_{i=1}^{4} h(i)|\chi_\varepsilon(1)\chi_\eta(2)\chi_\chi(3)\chi_\lambda(4)>$$

$$= h_{\mu\varepsilon}s_{\nu\eta}s_{\sigma\chi}s_{\rho\lambda} + s_{\mu\varepsilon}h_{\nu\eta}s_{\sigma\chi}s_{\rho\lambda} + s_{\mu\varepsilon}s_{\nu\eta}h_{\sigma\chi}s_{\rho\lambda} + s_{\mu\varepsilon}s_{\nu\eta}s_{\sigma\chi}h_{\rho\lambda} \tag{50}$$

where $h_{\mu\varepsilon} = <\chi_\mu|h|\chi_\varepsilon>$, etc. For the second term in (49), using the notation of (25),

$$<\chi_\mu(1)\chi_\nu(2)\chi_\sigma(3)\chi_\rho(4)|\sum_{i<j}^{4} \frac{1}{r_{ij}}|\chi_\varepsilon(1)\chi_\eta(2)\chi_\chi(3)\chi_\lambda(4)>$$

$$\begin{aligned} &= (\mu\varepsilon|\nu\eta)s_{\sigma\chi}s_{\rho\lambda} + (\mu\varepsilon|\sigma\chi)s_{\nu\eta}s_{\rho\chi} + (\mu\varepsilon|\rho\lambda)s_{\nu\eta}s_{\sigma\chi} \\ &\quad + s_{\mu\varepsilon}(\nu\eta|\sigma\chi)s_{\rho\lambda} + s_{\mu\varepsilon}(\nu\eta|\rho\lambda)s_{\sigma\chi} + s_{\mu\varepsilon}\sigma_{\nu\eta}(\sigma\chi|\rho\lambda) \end{aligned} \tag{51}$$

Once the single particle overlap, hamiltonian matrix elements and two electron integrals have been specified, the four-electron overlap and hamiltonian matrix elements between any two VB functions can be easily calculated.

Semi-Empiric Integral Approximations

In these semiempirical calculations, the only quantities obtained analytically from the basis AO's were the overlap integrals $s_{\mu\nu}$ between two AO's X_μ and X_ν and the one-center nuclear attraction ingetrals. The overlap integrals were calculated by the formulae given by Mullikan, et. al., (77) for overlaps among 1s, 2s, 2p, 3s and 3p Slater orbitals after the corrections according to Mullikan (78) were applied.

The one-center nuclear attraction integrals $\int \frac{\chi_\mu(i)\chi_\mu(i)}{R_{i\mu}} d\tau_i$ are easily evaluated by substituting the general form of the Slater orbital as given by (9) into the experssion and carrying out the indicated integration over all space it is seen that

$$\int \frac{\chi_\mu(R)\ \chi_\mu(R)}{R} d\tau = \frac{\zeta}{n} \tag{52}$$

where ζ is the Slater coefficient in the exponential argument of χ_μ.

The general element $h'_{\mu\nu}$ of the one particle hamiltonian matrix

$$h'_{\mu\nu} = <\mu|-\tfrac{1}{2}\nabla^2 + V_1 + V_2 + V_3|\nu> \tag{53}$$

and can be written as

$$h'_{\mu\nu} = <\mu|-\tfrac{1}{2}\nabla^2 + V_\nu|\nu> + \sum_{\gamma=1}^{3} <\mu|V_\gamma|\nu> - <_\mu|V_\nu|\nu> \tag{54}$$

where the last term merely cancels with the same term which occurs in the sum over the atomic centers.

The individual integrals were evaluated semiempirically using the following approximations. For χ_ν being any other AO except the one on center 3, the lone pair orbital,

$$<\mu|-\tfrac{1}{2}\nabla^2 + V_\nu|\nu> \simeq - I_\nu S_{\mu\nu} \tag{55}$$

the approximation used by Pohl, Rein and Appel (23) in their work on the hydrogen halides where I_ν is the experimental valence state ionization potential of the νth center. When χ_μ is identical to χ_ν, i.e. $S_{\mu\nu} = 1$, this reduces to

$$<\nu|-\tfrac{1}{2}\nabla^2 + V_\nu|\nu> \;=\; - I_\nu \tag{56}$$

the approximation used by Goeppert-Mayer and Sklar (79) on the benz ring and by a great many authors since, for singley ionized atoms. In the case where $\nu = 3$, i.e. the lone pair AO, a term was added to take account of the higher nuclear attraction. The approximation used was

$$<\mu|-\tfrac{1}{2}\nabla^2 + V_3|3> \simeq - [I_3 + (33|33)]S_{\mu 3} \tag{57}$$

after the work of Mickish and Pohl on O-H••O, N-H••N, and F-H••F (26). For $\mu = 3$, Equation (57) becomes

$$<3|-\tfrac{1}{2}\nabla^2 + V_3|3> \simeq - [I_3 + (33|33)] \tag{58}$$

which is the approximation for lone-pair orbitals used by Rein and Harris in their work on the N-H••N bond in the guanine-cytosine base pair (65).

Equations (55) and (56) imply an eigenvalue equation

$$(-\tfrac{1}{2}\nabla^2 + V_\nu)\ \chi_\nu = E_\nu\chi_\nu \tag{59}$$

where E_ν is the energy of the electron in the isolated atom in its valence state. For an atom contributing one electron to the bond this energy is taken to be the negative of the energy necessary to just remove the electron from the atom, i.e., $-I_\nu$. For the lone pair of electrons $-E_\nu$ is interpreted to be the ionization potential of the electron minus the coulomb interaction with the other electron occupying the orbital.

The remaining potential terms in Equation (54) were evaluated with the use of Mullikan's approximation (79) which replaces the electronic distribution $\chi_\mu \chi_\nu$ by $\frac{1}{2} S_{\mu\nu}(\chi_\mu \chi_\mu + \chi_\nu \chi_\nu)$. For the three center integral the application of this approximation yields

$$<\mu|V_\gamma|\nu> \simeq \tfrac{1}{2} S_{\mu\nu} \, [<\mu|V_\gamma|\mu> + <\nu|V_\gamma|\nu>] \qquad (60)$$

Each of the two center terms on the right hand side of Equation (60) was approximated to be

$$\begin{aligned} <\mu|V_\gamma|\mu> &\simeq <\mu| - \frac{Z_\gamma}{R_{\gamma i}} |\mu> \\ &\simeq - Z_\gamma / R_{\gamma\mu} \end{aligned} \qquad (61)$$

where Z_γ is the formal charge on center γ and $R_{\gamma\mu}$ is the separation between centers γ and μ.

The two center integrals such as $<\mu|V_\nu|_\nu>$ and $<\mu|V_\mu|\nu>$ were also subjected to the Mullikan approximation and were evaluated as

$$<\mu|V_\nu|\nu> \simeq \tfrac{1}{2} S_{\mu\nu} \, [<\mu|V_\nu|\mu> + <\nu|V_\nu|\nu>]$$

and

$$<\mu|V_\mu|\nu> \simeq \tfrac{1}{2} S_{\mu\nu} \, [<\mu|V_\mu|\mu> + <\nu|V_\mu|\nu] \quad . \qquad (62)$$

The one-electron hamiltonian matrix defined by Equation (54) is not hermitian when evaluated by the straightforward use of the above approximations. This is easily seen by writing down the elements $h'_{\mu\nu}$ and $h'_{\mu\nu}$,

$$h'_{\mu\nu} = - I_\nu S_{\mu\nu} + \sum_{\gamma=1}^{3} <\mu|V_\gamma|\nu> - \tfrac{1}{2} S_{\mu\nu} \, [<\mu|V_\nu|\mu> + <\nu|V_\nu|\nu>] \qquad (63)$$

and

$$h'_{\mu\nu} = - I_\mu S_{\nu\mu} + \sum_{i=1}^{3} \langle\mu|V_\gamma|\nu\rangle - \tfrac{1}{2}S_{\nu\mu} \left[\langle\nu|V_\mu|\nu\rangle + \langle\mu|V_\mu|\mu\rangle\right]$$

These elements are clearly not the same for $\mu \neq \nu$ but must be so as to insure real eigenvalues. To avoid the difficulty a new matrix $\mathfrak{h}$ was defined and used such that

$$h_{\mu\nu} = \tfrac{1}{2}(h'_{\mu\nu} + h'_{\nu\mu}) \ . \qquad (64)$$

The new matrix element $h_{\mu\nu}$ is then

$$\begin{aligned} h_{\mu\nu} = & -\tfrac{1}{2} S_{\mu\nu} \left[I_\mu + I_\nu\right] + \tfrac{1}{2} \sum_{\gamma=1}^{3}\left[\langle\mu|V_\gamma|\nu\rangle + \langle\nu|V_\gamma|\mu\rangle\right] \\ & - \tfrac{1}{4} S_{\mu\nu} \left[\langle\mu|V_\nu|\mu\rangle + \langle\nu|V_\nu|\nu\rangle + \langle\mu|V_\mu|\mu\rangle + \langle\nu|V_\mu|\nu\rangle\right] \end{aligned} \qquad (65)$$

For μ or ν being 3, I_μ or I_ν in the first term of the right hand side is replaced by $I_3 + (33|33)$. This approximation was used also by Pohl and co-workers (23-26) in their semiempiric calculations.

The two electron integrals were reduced to linear sums of one and two center coulomb integrals with Mullikan's approximation. For a multi-centered integral $(\mu\nu|\lambda\sigma)$ this results in the expression

$$(\mu\nu|\lambda\sigma) = \tfrac{1}{4}S_{\mu\nu} S_{\lambda\sigma} \left[(\mu\mu|\lambda\lambda) + (\mu\mu|\sigma\sigma) + (\nu\nu|\lambda\lambda) + (\nu\nu|\sigma\sigma)\right] \qquad (66)$$

The two center coulomb integrals were estimated by the Pople point charge approximation (6) as

$$(\mu\mu|\nu\nu) = \frac{1}{R_{\mu\nu}} \qquad (67)$$

while the one center integrals were taken to be

$$(\mu\mu|\mu\mu) = I_\mu + A_\mu \qquad (68)$$

according to Pariser's suggestion (81) where A_μ is the valence state electron affinity.

Values for the ionization potentials and electron affinities used in the semi-empiric calculations were obtained from the preprint of the paper by Hinze and Jaffe (82) on the negativities of neutral atoms. In the cases of F and Cl, it was necessary to estimate the ionization potentials and electron affinities as these values were not given for the tetrahedral valence state. The estimations were made following a suggestion by Pohl (83) in the following manner.

The relationships between the valence state state ionization potential I_ν and electron affinity A_ν and the ground state values Ig and Ag are (82)

$$\begin{aligned} I_\nu &= Ig + P_+ - P_o \\ A_\nu &= Ag + P_o - P_- \end{aligned} \tag{69}$$

where P^+, P^o, and P^- are respectively the energies necessary to promote the positive ion from its ground state to the valence state, the neutral atom from the ground state to the valence state, and the negative ion from the ground state to the valence state. Hinze and Jaffe list P_+ for F and Cl in the tetrahedral state but not P_o or P_-. P_o was obtained by comparing the value given by a graphical extrapolation of P_{+++}, P_{++} and P_+ the promotion energy for the tripley ionized atom, etc. of the tetrahedral states of highest pairing and the value obtained by a similar extrapolation of the P_o's of the directly preceding elements of the periodic table. An average of these was taken as the energy used. Two analogous extrapolations were used to obtain values for P_-. The values obtained for P_o and 7 ev for F and 5.5 ev for Cl. P_- was estimated to be 2.9 ev for F and 4.0 ev for Cl.

In the split shell calculations, the addition of the hydrogen 2p AO made necessary the analytic evaluation of the two coulomb integrals $(1s_H 1s_H | 2p_H 2p_H)$ and $(2p_H 2p_H | 2p_H 2p_H)$. These were calculated to be 0.328125 and).19570 with the formulas given by Roothaan (84). For consistency within the program, an effective electron affinity was obtained from $(2p_H 2p_H | 2p_H 2p_H)$ and the energy of $2p_H$ state and read into the computer with the rest of the data and the integral then computed each time as the other were.

The core-core repulsion energies were calculated by a modification of the method used by Mickish and Pohl (26) in their work on N-H••N, O-H••O, and F-H••F. For a given geometric configuration the core-core repulsion energies are written as the sum of repulsion energies between each pair of centers, i.e.

$$E_{cc} = V_{12} + V_{13} + V_{23} \qquad (70)$$

V_{13} was calculated as the coulomb repulsion between two point charges using the formal charges assigned to the centers, i.e.

$$V_{13} = \frac{2}{R_{13}} \qquad (71)$$

V_{12} and V_{23} were constructed to include the effect of the proton penetrating the electronic charge clouds shielding the nuclei of centers 1 and 3. This was accomplished by assuming that the repulsion due to center α experienced by the proton is of the form

$$V_{\alpha 2} = \frac{Z_{\alpha}^{eff}(R_{\alpha 2})}{R_{\alpha 2}} \qquad (72)$$

where Z_{α}^{eff} has a value between the formal charge assigned to the atomis core and the full nuclear charge of the atom. To evaluate

$Z_\alpha^{eff}(R)$ Mickish and Pohl used the form

$$Z_\alpha^{eff}(R) = Z_\alpha^{core} + (Z_\alpha^{Nuc} - Z_\alpha^{core}) \exp\,[-2\lambda_\alpha' R_{\alpha 2}] \qquad (73)$$

where Z_α^{nuc} is the total nuclear charge of center α and λ_α' is obtained by use of Herman and Skillman's tables of the potential energy of an electron in the field of an atom (85). λ_α' was found by picking a value of the potential, V_{HS}, from the tables for a distance R_{HS} of about .5 au. An effective Z^{HS} was determined by

$$Z_\alpha^{HS} = V_{HS} R_{HS}$$

and a λ' by

$$\lambda' = -\frac{1}{2}\frac{1}{R_{HS}} \ln\left[\frac{Z_\alpha^{Nuc} - Z_\alpha^{core}}{Z_\alpha^{HS} - Z_\alpha^{core}}\right] . \qquad (74)$$

The equilibrium values of R_{XH} that Mickish and Pohl obtained using values for the shielding parameter R_X' as defined above were too large, some by so much as .3 au. To correct this a new λ_α was employed such that

$$\lambda_\alpha = \left[\frac{Z_\alpha^{Nuc} - S_{n-v}}{Z_\alpha^{Nuc} - S_n}\right] \lambda_\alpha' \qquad (75)$$

where S_n is the Slater shielding constant (73) for center α with n electrons in the outer shell and S_{n-v} is the shielding constant of the center when v electrons have been contributed to the bonding MO's.

The rationale for this device is that the delocalization of the bonding electron from the AO into the MO allows the remaining electrons to be pulled in closer to the nucleus since each is subjected to a diminished shielding. Equation (75) is an intuitive if not strictly logical way of correcting for this. A sketch of the behavior of the two relations for Z_α^{eff} is sketched in Figure 2. The curves are labeled by their respective shielding coefficients.

This completes the specification of the approximations for the RDAO-1 calculations. The experimental values, orbital coefficients, and shielding parameters used for integral evaluations are shown in Table II.

TABLE II

PHYSICAL CONSTANTS, ORBITAL EXPONENTS, AND SHIELDING PARAMETERS

Valence State	Slater Orbital Exponent	Valence State Ionization Potential (a.u.)	Valence State Electron Affinity (a.u.)	Screening Parameter $\lambda'\alpha$ (a.u.)	Screening Constant (Slater) Sn	Screening Constant (Slater) Sn-v
H(1S)	1.000	0.5000	-0.0276	- - -	- - -	- - -
H(2p)	0.500	0.1250	+0.7070	- - -	- - -	- - -
$\mathrm{N(te^{2}tete\underline{te})}$	1.950	0.6962	-0.1490	0.9286	3.10	2.40
$\mathrm{N(\underline{te}^{2}tetete)}$	1.950	0.5163	-0.1490	1.2999	3.10	2.40
$\mathrm{O(te^{2}te^{2}te\underline{te})}$	2.275	0.8969	-0.2247	0.9865	3.45	3.10
$\mathrm{O(te^{2}\underline{te}^{2}tete)}$	2.275	0.6879	-0.2247	1.3266	3.45	3.10
$\mathrm{F(te^{2}te^{2}te^{2}\underline{te})}$	2.600	0.9230	-0.2200	1.0666	3.80	3.80
$\mathrm{F(te^{2}te^{2}\underline{te}^{2}te)}$	2.600	0.7470	-0.2200	1.3856	3.80	3.80
$\mathrm{P(te^{2}tete\underline{te})}$	1.600	0.5359	-0.1192	1.1232	10.20	9.50
$\mathrm{P(\underline{te}^{2}tetete)}$	1.600	0.4410	-0.1192	1.2998	10.20	9.50
$\mathrm{S(te^{2}te^{2}te\underline{te})}$	1.817	0.5701	-0.1754	1.1335	10.55	10.20
$\mathrm{S(te^{2}te^{2}tete)}$	1.817	0.5017	-0.1754	1.2962	10.55	10.20
$\mathrm{Cl(te^{2}te^{2}te^{2}\underline{te})}$	2.033	0.5850	-0.1909	1.1331	10.90	10.90
$\mathrm{Cl(te^{2}te^{2}\underline{te}^{2}te)}$	2.033	0.4992	-0.1909	1.2884	10.90	10.90

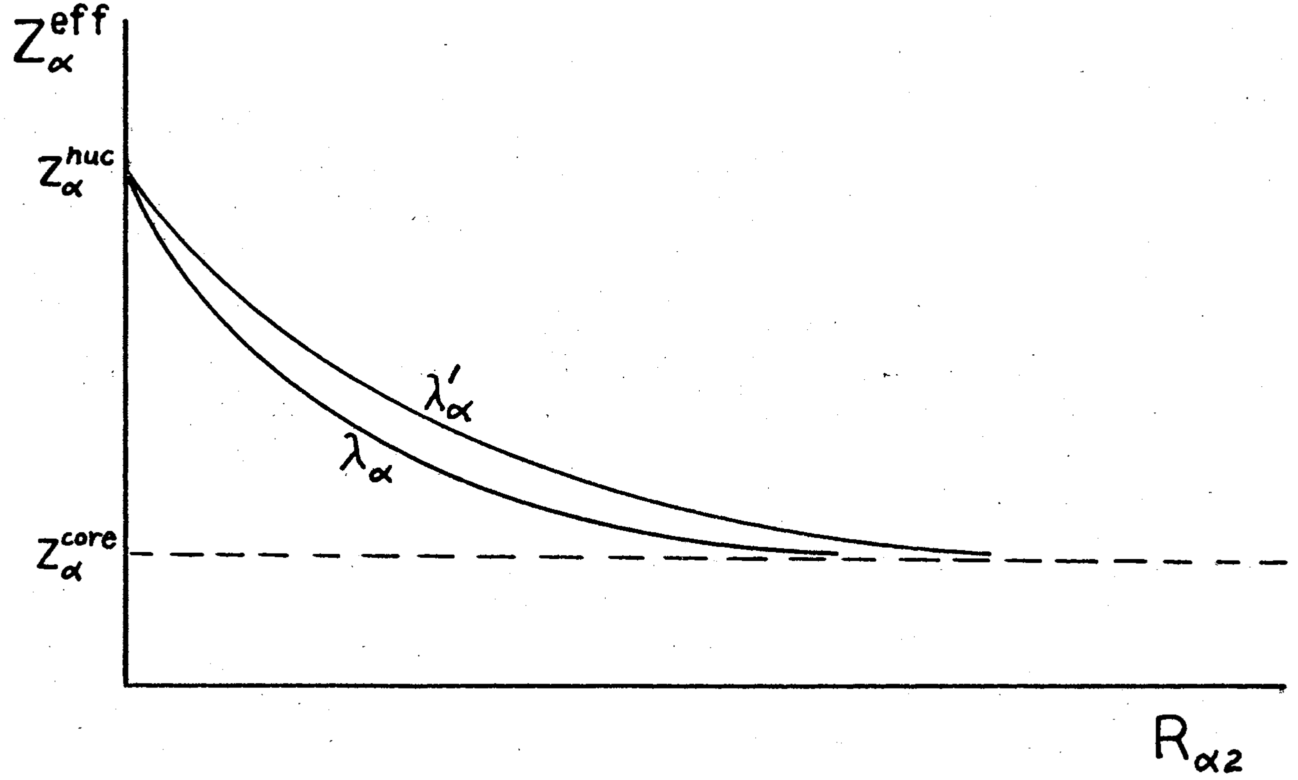

Figure 2. Z_α^{eff} as Functions of Screening Parameters

CHAPTER III

RDAO-1 CLOSED SHELL CALCULATIONS AND RESULTS

Calculations of the total energy of the system for several X••Y separations for each of twenty-one separate systems X-H••Y using the Roothaan SCF procedure described in Chapter II. For X being N, O, or F, Y was taken to be N, O, F, S, and Cl while for X being Cl, Y was taken to be N, O, F, and Cl. Additional calculations were made on the P-H••P systems and the S-H••S systems. From these, binding energies as a function of the X••Y separation, X-H and X••Y equilibrium distances, and force constants were obtained as is described in later sections of this chapter.

Computation Details

The SCF calculations were performed, using a modified version of a program originally written by D. J. Mickish (86) in the FORTRAN IV language for the IBM 7040 computer. Two subroutines from the Quantum Chemistry Program Exchange were used to solve the secular equation of the Roothaan procedure. These subroutines were CEIG written by Michels, van Dine, and Elliot (87) and GIVENS written by Prosser (88). Both subroutines were written for the IBM 7090 computer and had to be converted to double precision accuracy for the IBM System 360 in order for them to yield accurate answers for the test data supplied with the subroutines. The overlap integrals between AO's were computed in a separate subroutine using the formulas developed by Mullikan, et. al. (77). For any overlap involving an AO with a principal quantum number of 3 it was necessary for this subroutine to also be written in doubld precision arithmetic in order for the answers to check with the table of values in reference (77). The convergence criterion employed was that each coefficient varied by less than 0.001 from the value of the immediately preceding cycle. If convergence was not reached in 30 iterations, R_{12} was incremented to the next point. A calculation on O-H··O system allowing a varience of only 0.0001 was also made but gave the same energy values to five decimal places. As the ionization potentials used as input parameters were given to only four decimal places, the varience criterion of 0.001 was used in all subsequent calculations.

A second order extrapolation procedure devised by Mickish (86) was employed to help speed convergence. This was a parabolic approximation scheme in which three points are assumed to lie on a parabola and to be equally spaced along the x-axis.

If y_1, t_2, and y_3 are known and $x_1-x_2=x_2-x_3-x_4$, then using $y=y_4+b(x-x_4)+a(x-x_4)^2$, y_4 is given by

$$y_4 = 3y_3 - 3y_2 + y_1. \tag{76}$$

Using this form, a three step cycle was used in which the first iterations were simple eigenvector substitutions in which the MO coefficients used to begin the iteration were the coefficients obtained from the last iteration. For the start of the third iteration each coefficient $C_{i\nu}$ was approximated as

$$C_{i\nu}^{(3)*} = 3C_{i\nu}^{(3)} - 3C_{i\nu}^{(2)} - C_{i\nu}^{(1)} \tag{77}$$

where $C_{i\nu}^{(n)}$ is the coefficient calculated from the n-1 iteration in the cycle and the starred coefficient is the extrapolation used for the third step in the cycle.

Using this procedure, the calculation rarely took more than 12 iterations to converge. The average time taken for each point was approximately 1.6 sec. for the IBM 360/50 and 0.5 sec. for the IBM 360/65.

A preliminary calculation of the potential energy curve of the proton in the O-H··O system was made to test the range of validity of the integral approximations. The O-O separation was taken to be 5.00 au and the O-H distance was varied from 1.0 au to 4.0 au in increments of 0.25 au. The total energy vs. R_{12} is plotted in Figure 3 and the MO coefficients are given in Table III.

As seen from Figure 3, the closed shell description gives a local minimum at approximately the experimental equilibrium value of R_{12} = 1.91 au but exhibits anamolous behavior or both sides of this minimum. The rather percipitous plunge of the curves in the region between 3.0 and 4.0 au and the leveling out of the curves around R_{12} = 1 au indicates that the approximation give good behavior only in the equilibrium region of the proton position. This behavior of the energy curves renders invalid any search for a double well potential for the proton when these approximations are used.

The wavefunctions also show anamolous behavior in the same regions as do the proton potential energies. From Table III it is seen that the coefficient C_{12} of the closed shell function changes sign between O-H separations of 1.5 and 1.25 au and again between separations of 3.5 au and 4.0 au with no convergence of the wave function at all at R_{12} = 3.75 au after 30 iterations. The MO ψ_1 associated with the lowest

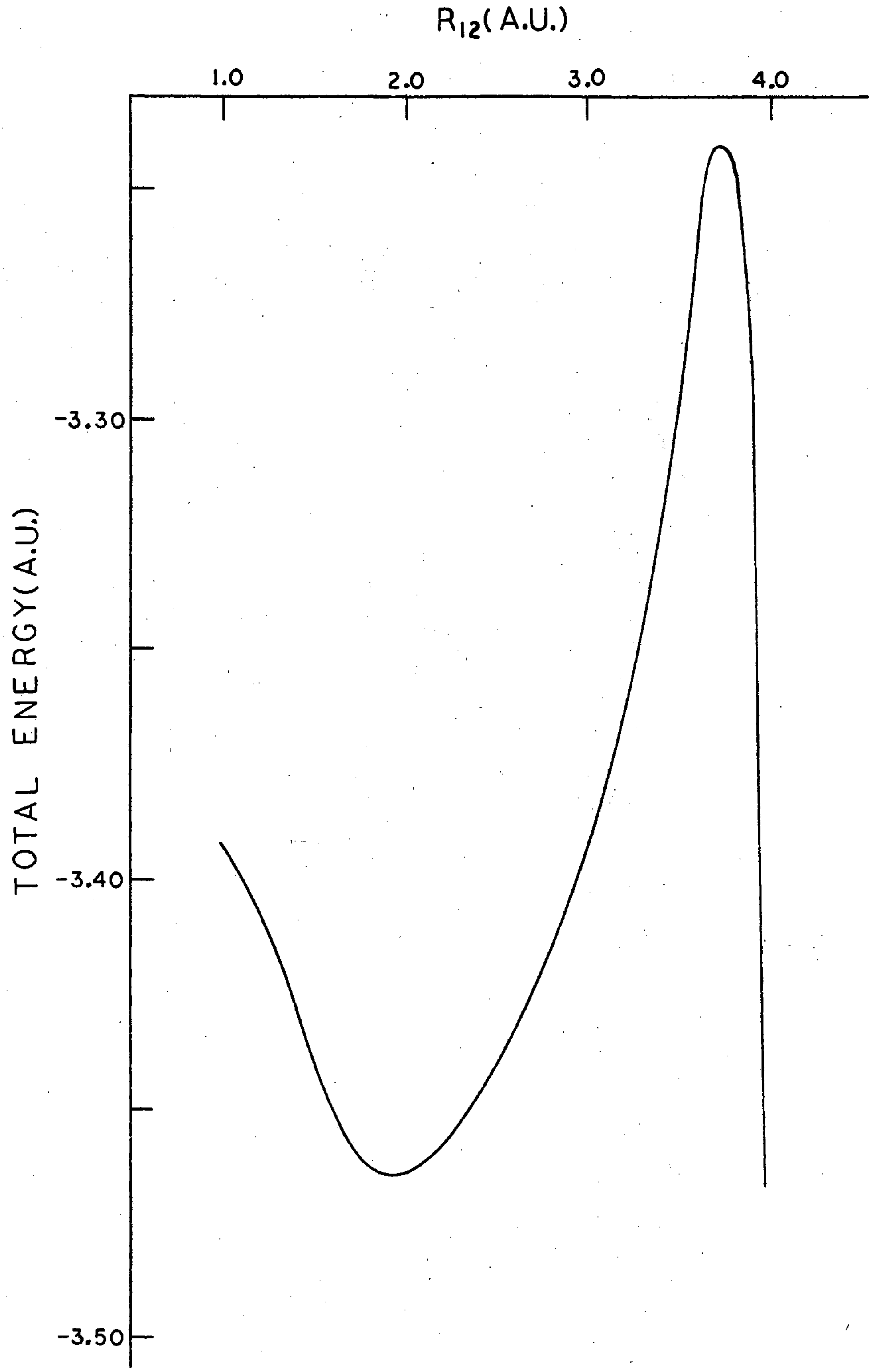

Figure 3. RDAO-1 SCF Total Energy vs. R_{12} for O-H··O for Extended Range of R_{12}

TABLE III

SCF ENERGY AND WAVEFUNCTION

R_{12}	E	C_{11}	C_{12}	C_{13}	C_{24}	C_{22}	C_{23}
1.00	-3.3924	1.2818	-0.4877	0.0291	.0037	- .0053	1.0005
1.25	-3.4113	1.1421	-0.2310	0.0236	-0.0327	-0.0330	.9955
1.50	-3.4394	0.9737	0.0165	0.1546	-0.2223	-0.0692	-0.9749
1.75	-3.4613	0.6129	0.1723	0.6395	-0.6862	-0.0167	0.7368
2.00	-3.4653	0.2981	0.21175	0.8357	0.8412	0.118	-0.4734
2.25	-3.4566	0.1739	0.2347	0.8627	0.8740	0.1601	-0.3738
2.50	-3.4405	0.1088	0.2572	0.8556	0.8963	0.1737	-0.3226
2.75	-3.4195	0.0689	0.2800	0.8349	0.9180	0.17183	-0.2875
3.00	-3.3928	0.04338	0.3041	0.8059	0.9381	0.1608	-0.2588
3.25	-3.3546	0.0274	0.3343	0.7677	0.9545	0.1465	-0.2352
3.50	-3.2920	0.0179	0.3951	0.7006	0.9657	0.1341	-0.2242
3.75	No Convergence						
4.00	-3.7017	0.0412	-1.2699	0.4508	1.0031	-0.0810	-0.5309

orbital energy has positive coefficients as would be expected only in the region of OH separation of 1.5 to 3.5 au. Because of this behavior of the energy attention in subsequent calculations was confined to regions around the experimental value of the proton position.

RDAO-1 Closed Shell Results

The lowest total energy of the system and the proton equilibrium position for a fixed X••Y separation were determined by plotting the five or six lowest energies obtained from the computer calculations against their respective values of R_{12}. A series of these curves resulted for each fragment X-H••Y and are shown in Figures 4-25. Each curve was obtained and a fixed value of R_{13} and is labeled with this value.

These curves exhibit some general characteristics which are qualitatively in accord with experiment. The systems for which the calculations predict binding show a barely perceptible to a quite noticeable increase in the equilibrium value of the X-H bond length while undergoing H-bonding. The curves for finite values of R_{13} except for the systems S-H••S and P-H••P also exhibit a slight to easily perceptible flattening around the equilibrium point indicating a decrease in the force constant for linear stretching vibrational mode. This is also in accordance with experiment.

The separation energies of the X-H••Y fragments were calculated as the difference between the minimum energy for infinite separation of the X-H fragment and the neutral Y center and the minimum total energy of X-H••Y for each finite value of R_{13}. These binding energies were plotted as functions of R_{13} to obtain the equilibrium energies and X••Y separations for each fragment. Figure 26 shows the binding energy vs.

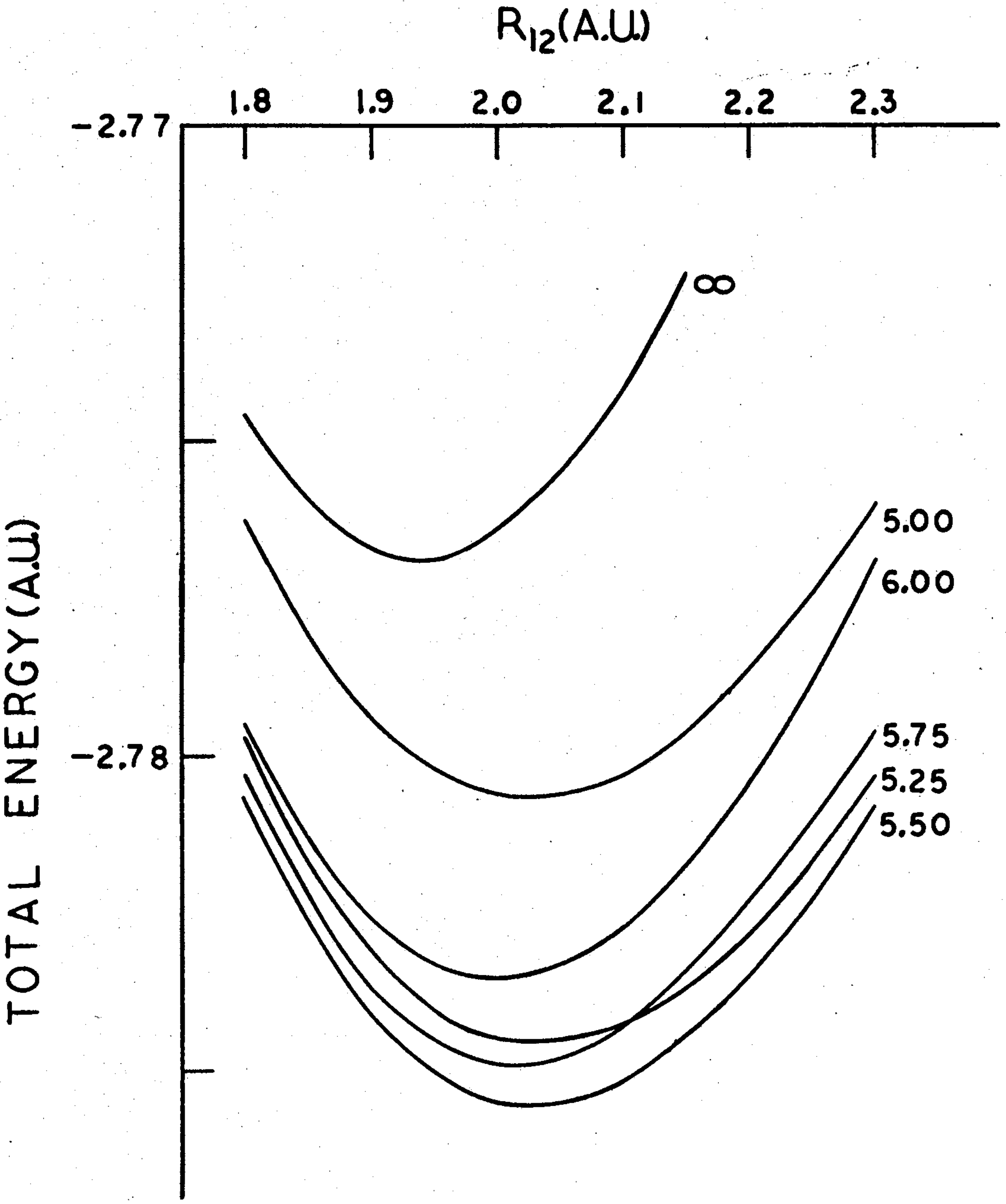

Figure 4. RDAO-1 SCF Energy vs. R_{12} for N-H··N

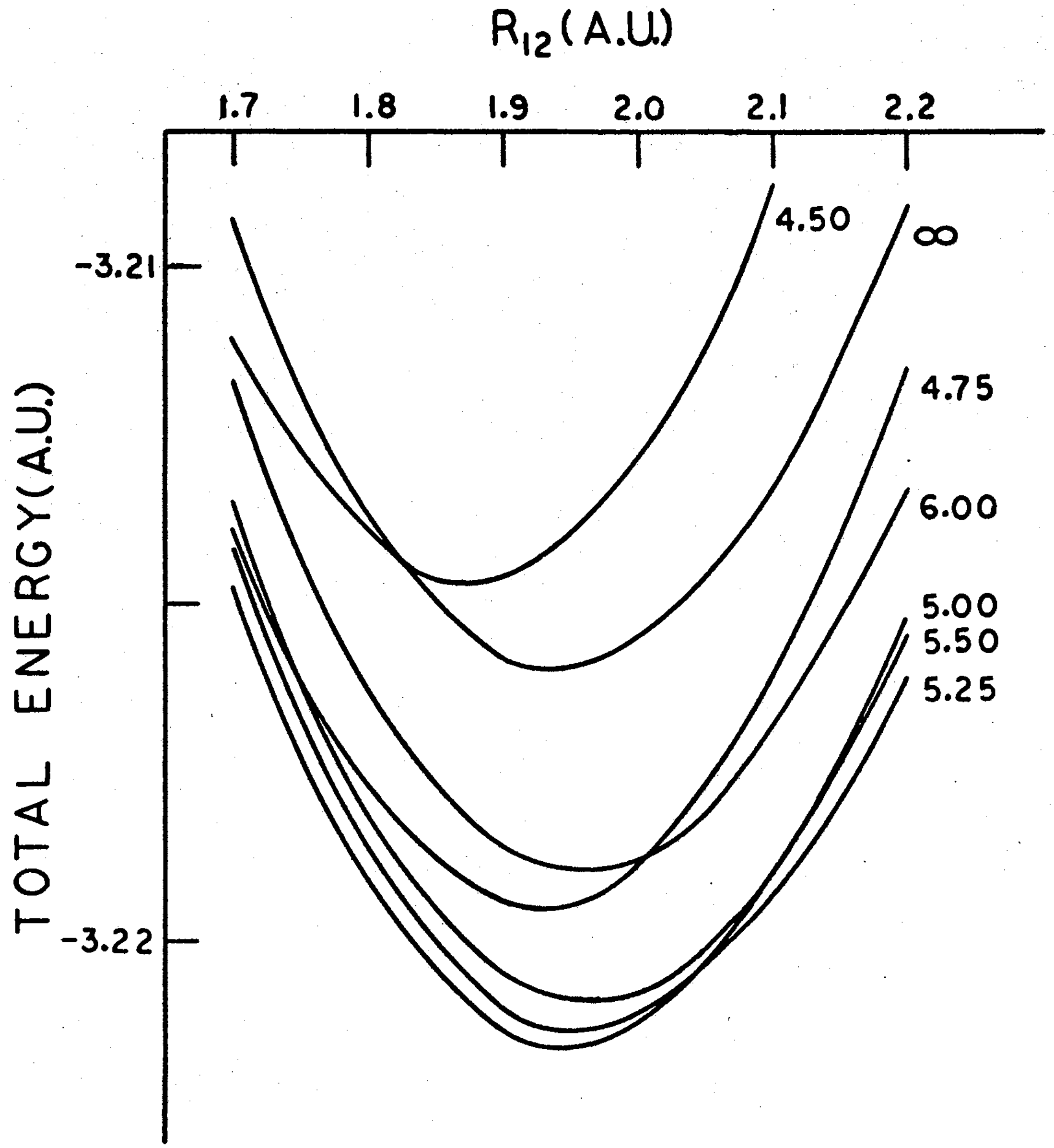

Figure 5. RDAO-1 SCF Energy vs. R_{12} for N-H··O

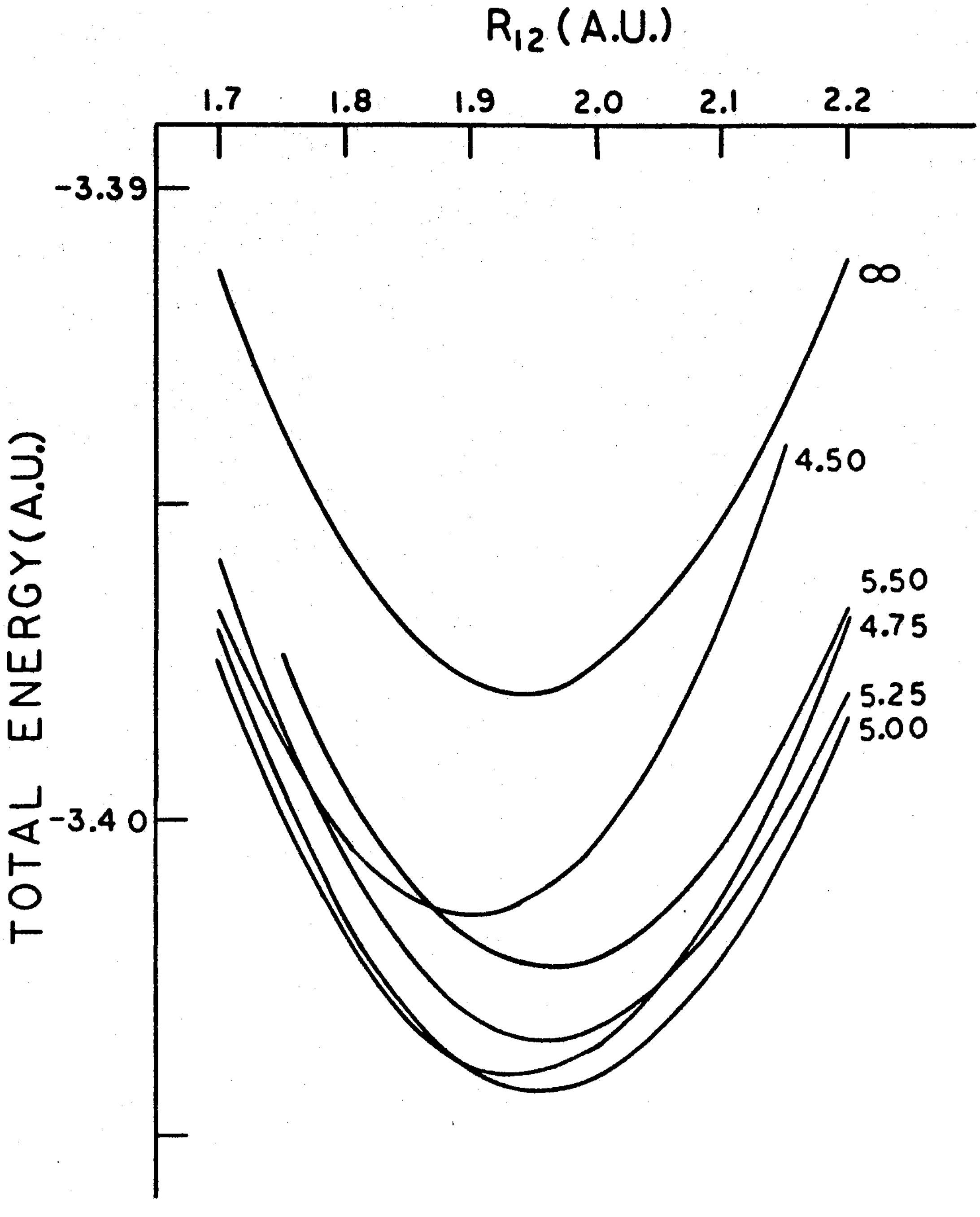

Figure 6. RDAO-1 SCF Energy vs. R_{12} for N-H··F

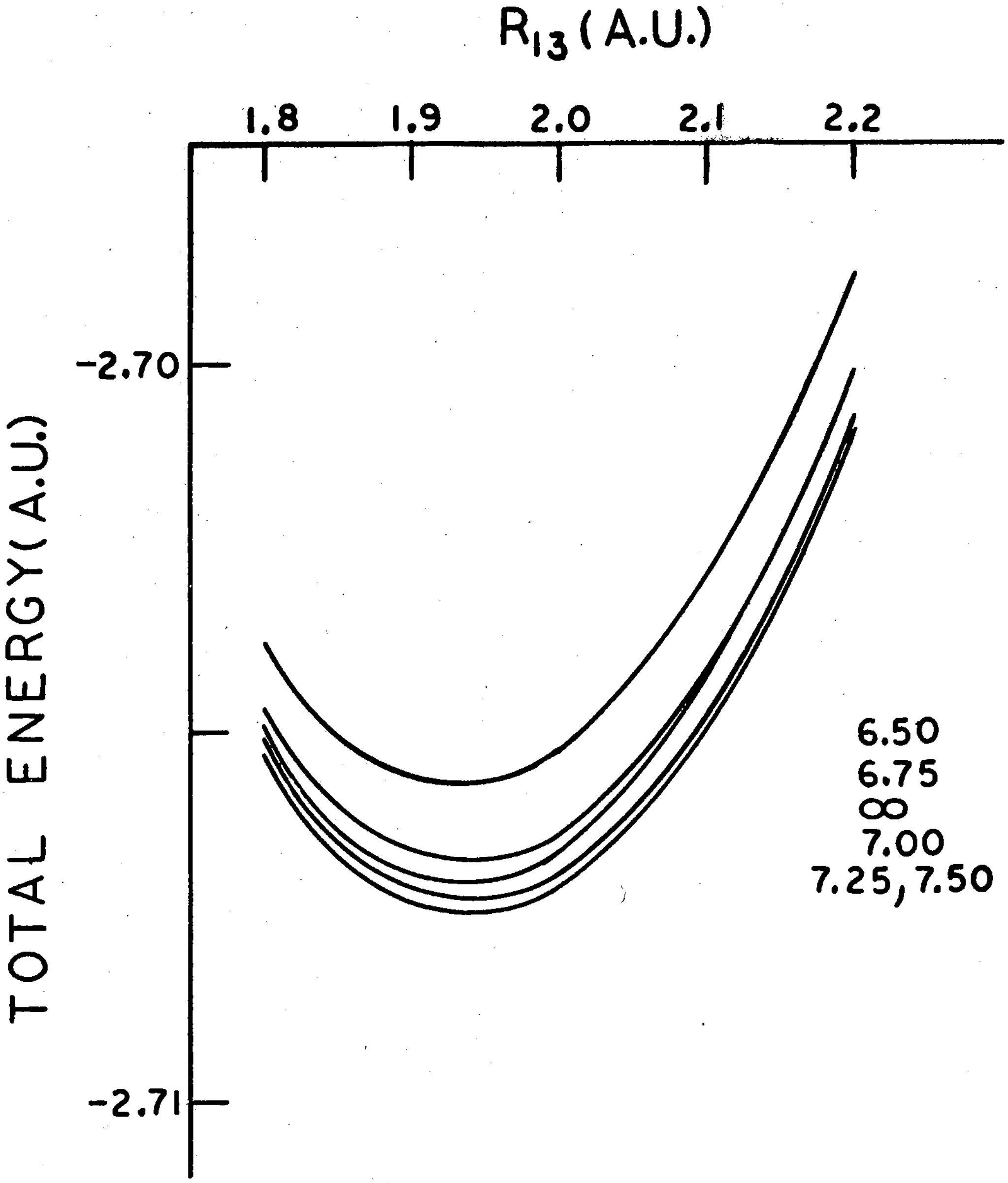

Figure 7. RDAO-1 SCF Energy vs. R_{12} for N-H··S

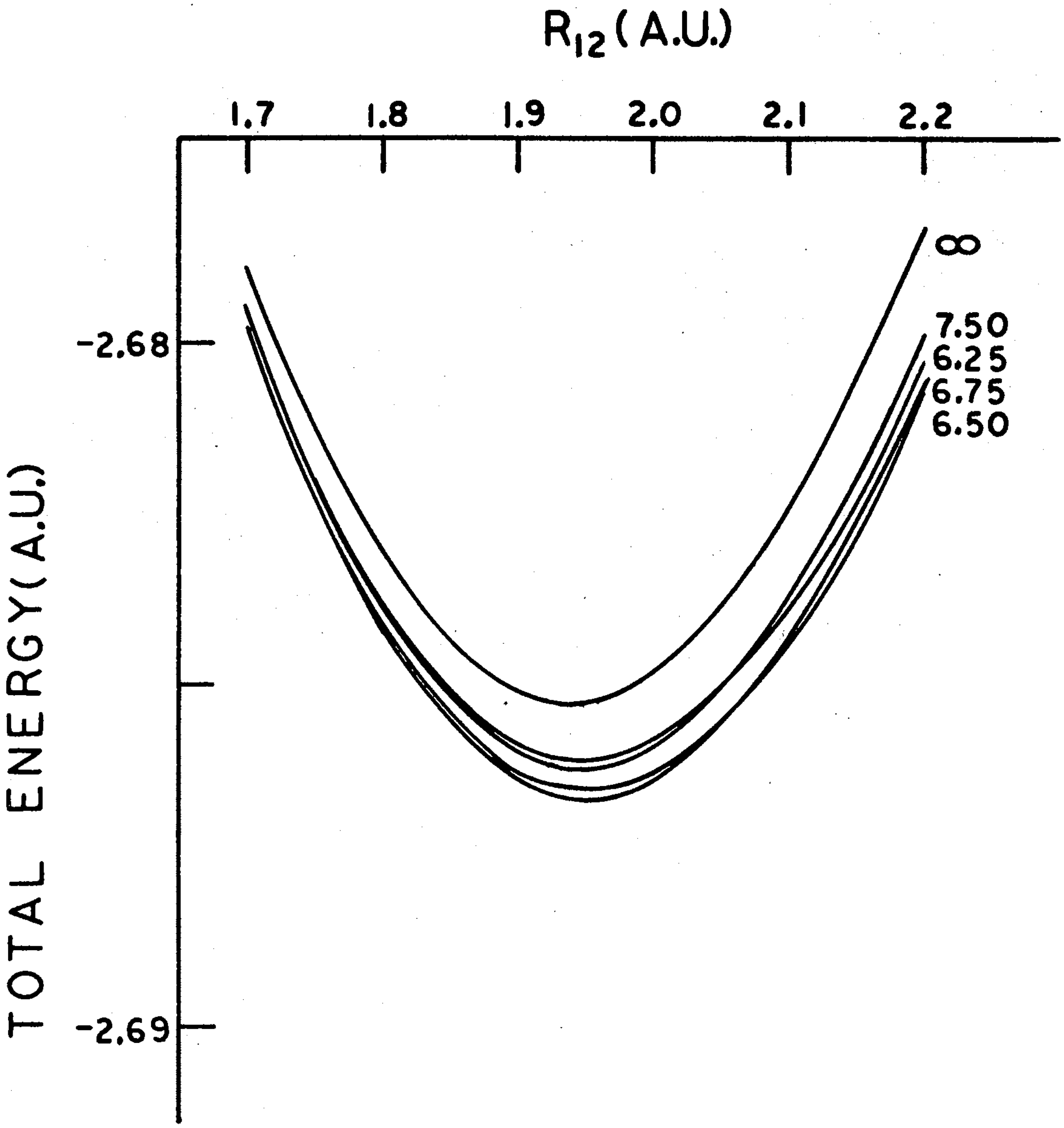

Figure 8. RDAO-1 SCF Energy vs. R_{12} for N-H⋅⋅Cl

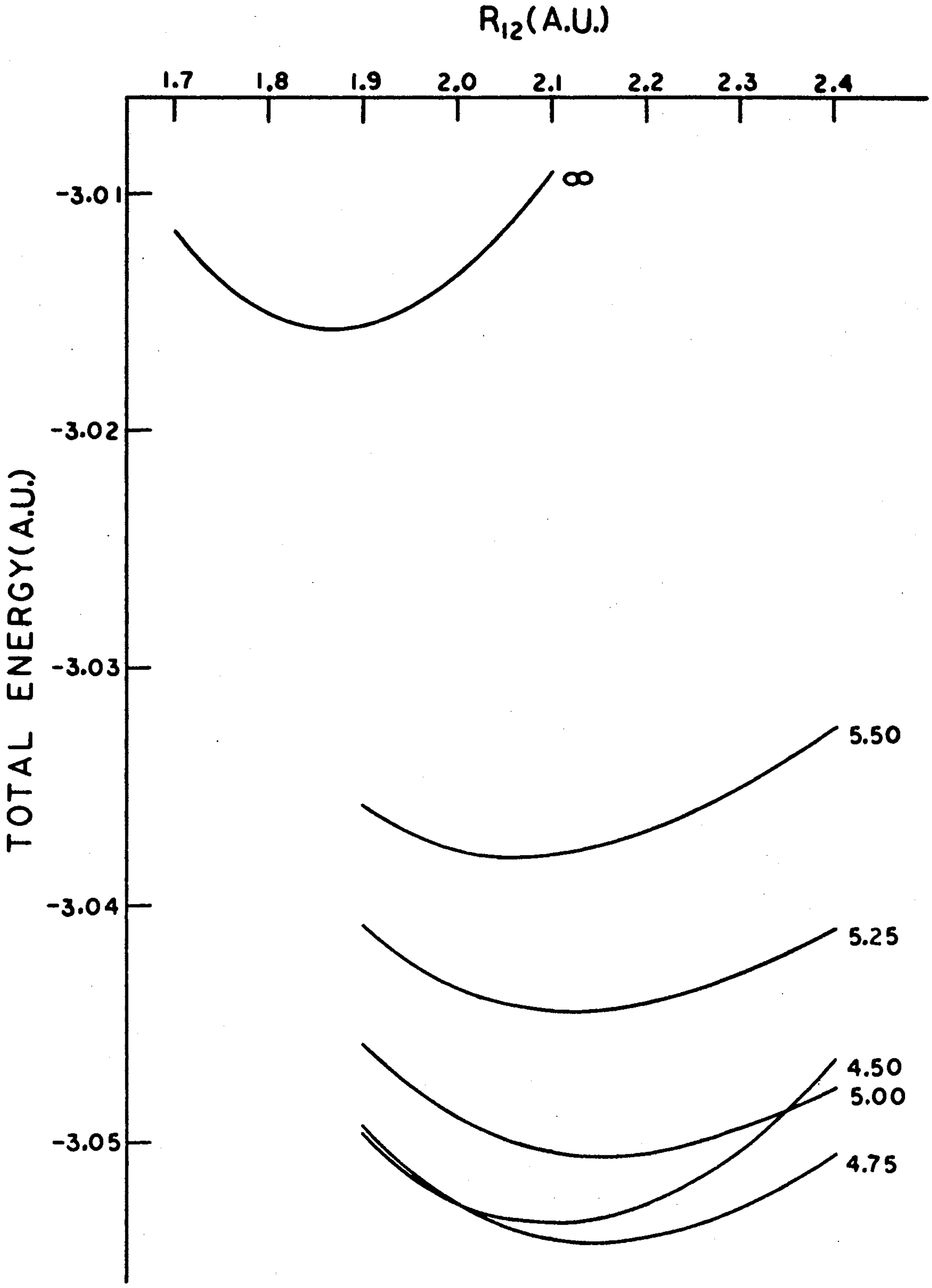

Figure 9. RDAO-1 SCF Energy vs. R_{12} for O-H··N

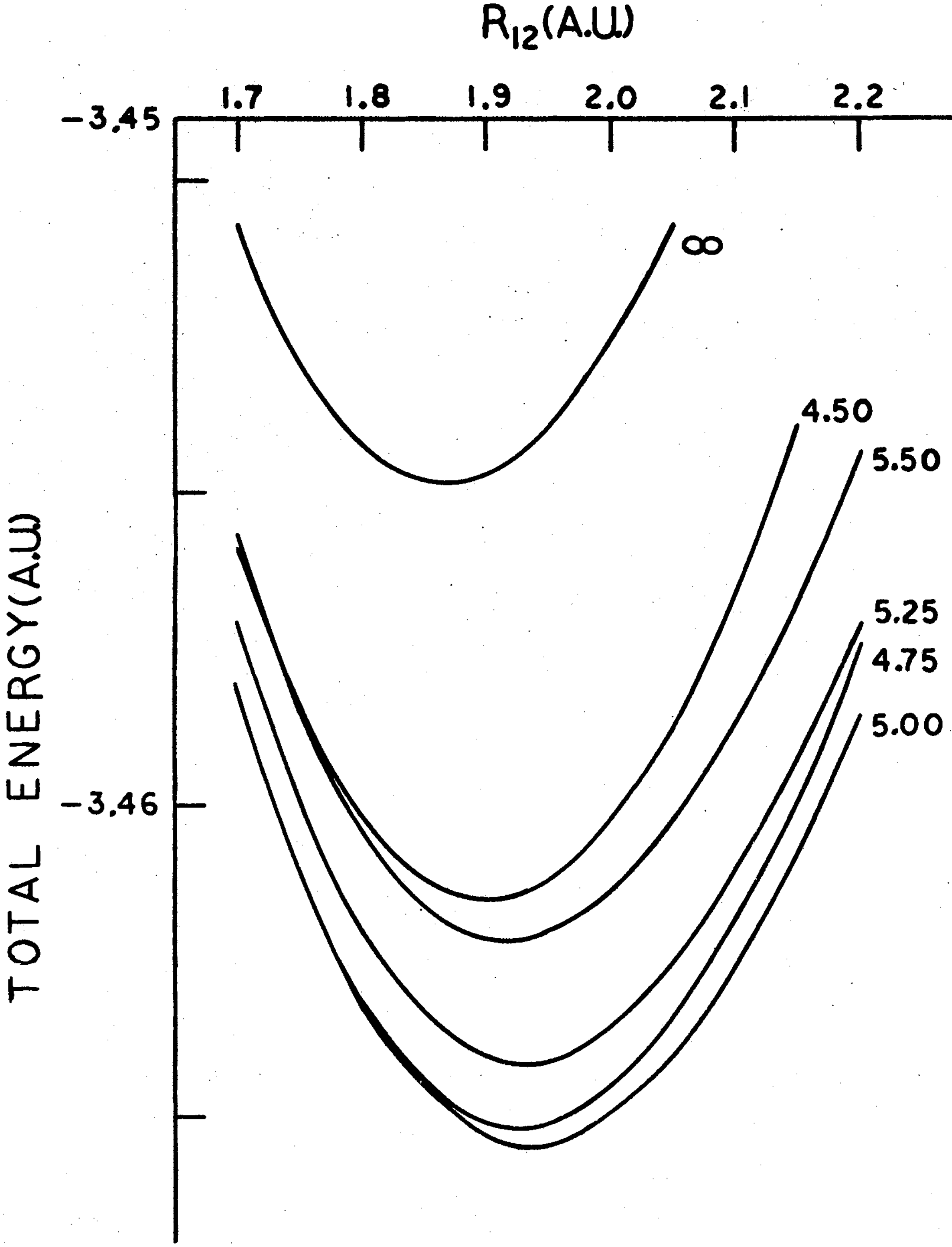

Figure 10. RDAO-1 SCF Energy vs. R_{12} for O-H∘∘O

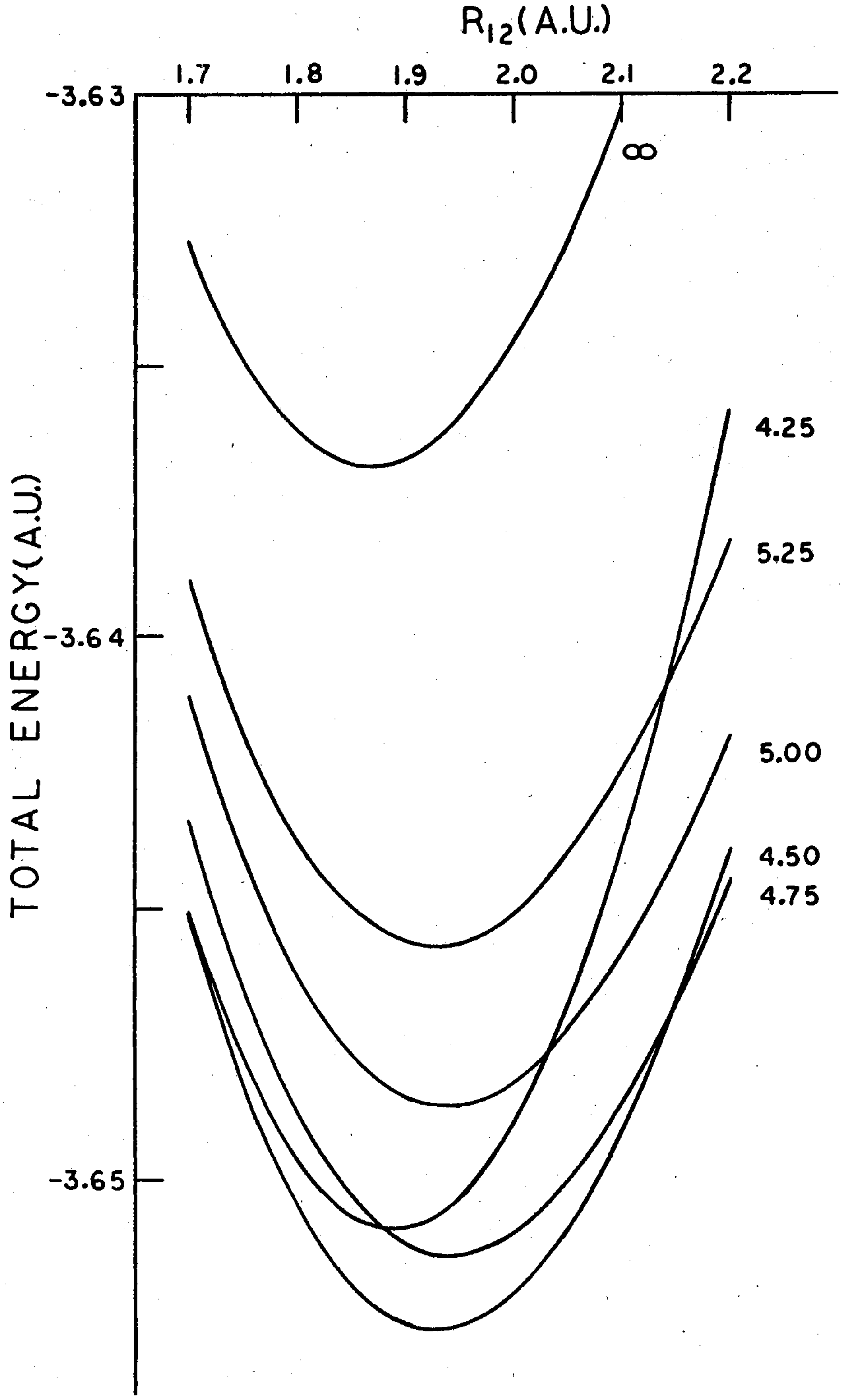

Figure 11. RDAO-1 SCF Energy vs. R_{12} for O-H··F

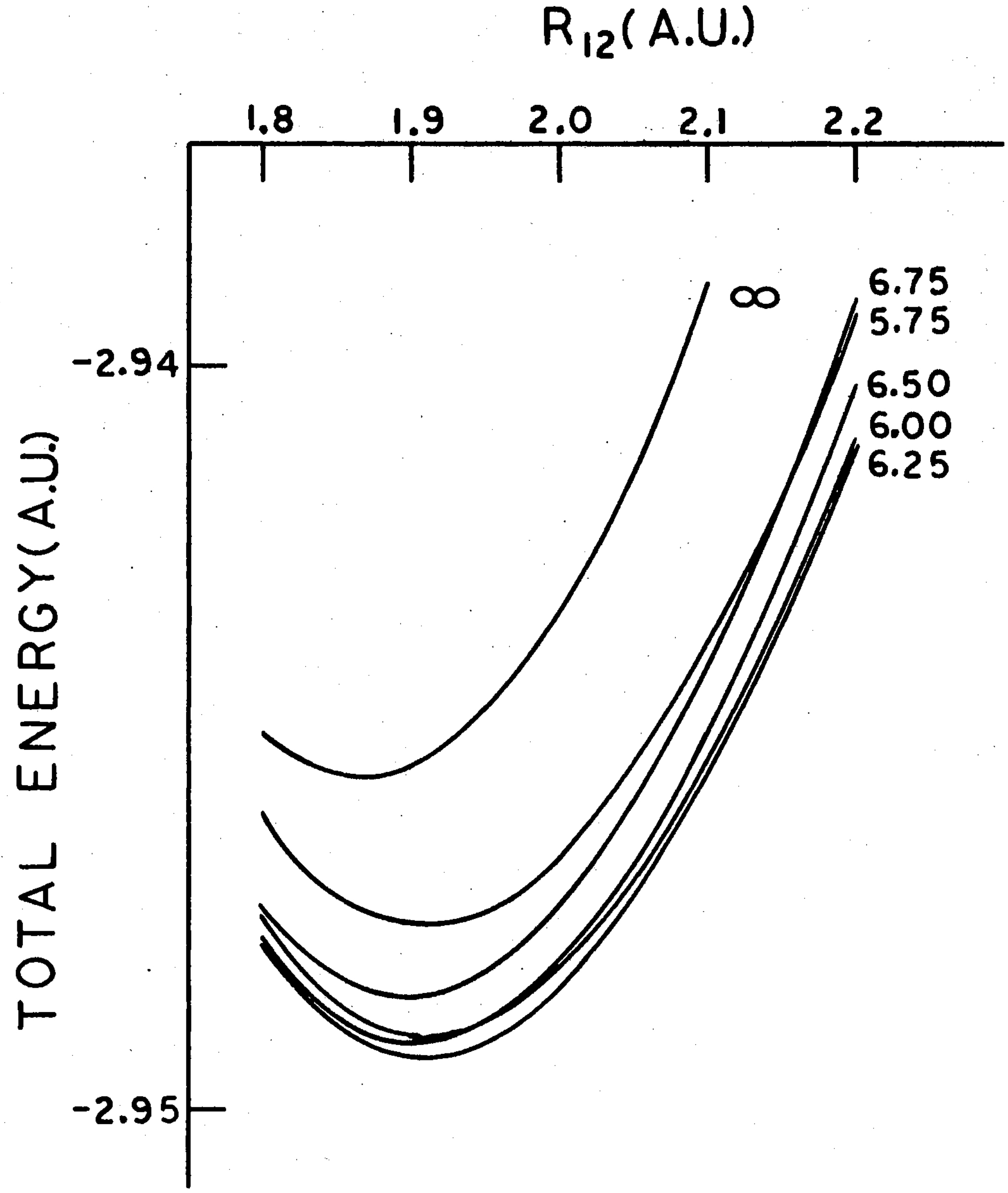

Figure 12. RDAO-1 SCF Energy vs. R_{12} for O-H··S

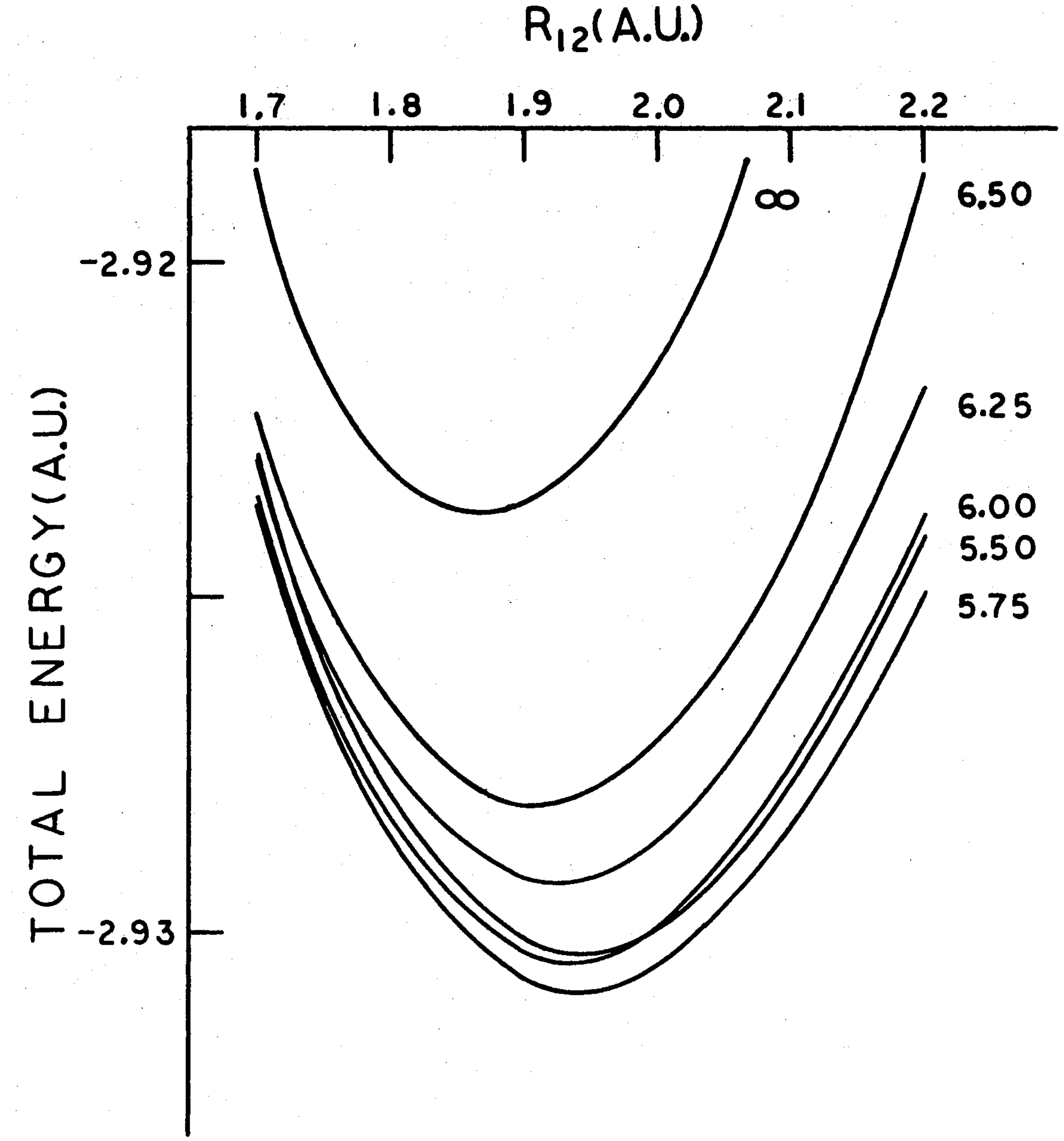

Figure 13. RDAO-1 SCF Energy vs. R_{12} for O-H∘∘Cl

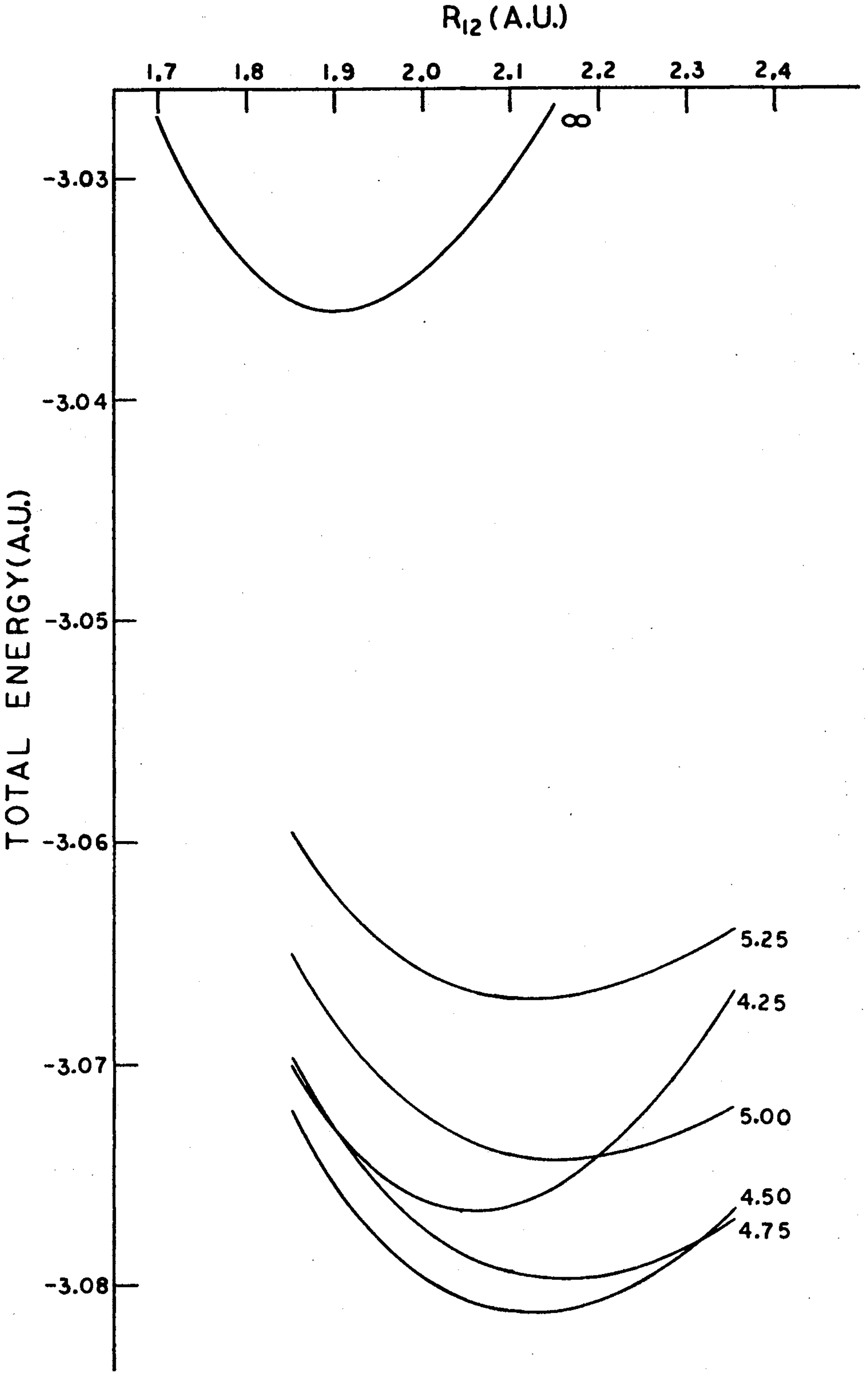

Figure 14. RDAO-1 SCF Energy vs. R_{12} for F-H∘∘N

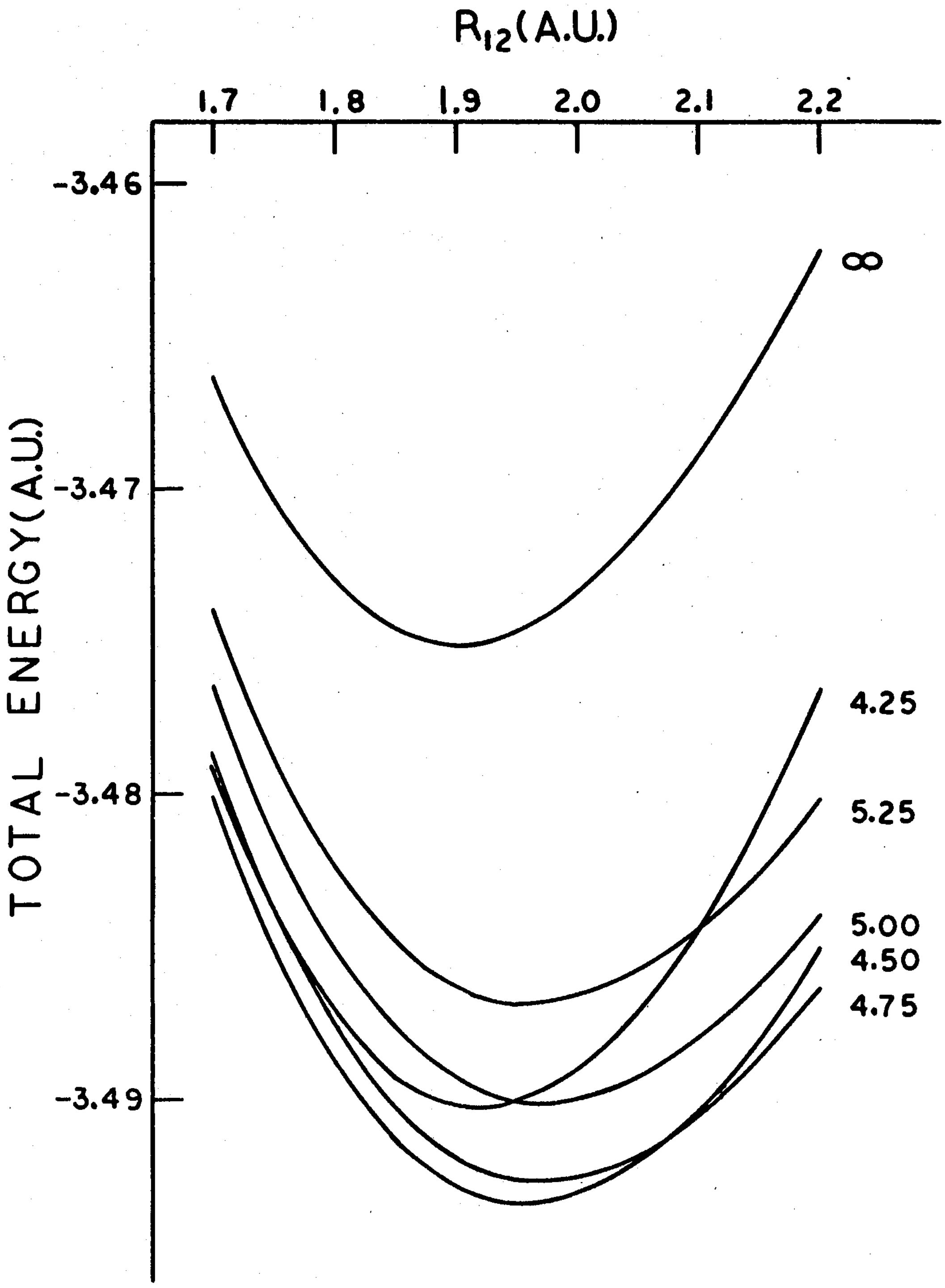

Figure 15. RDAO-1 SCF Energy vs. R_{12} for F-H··O

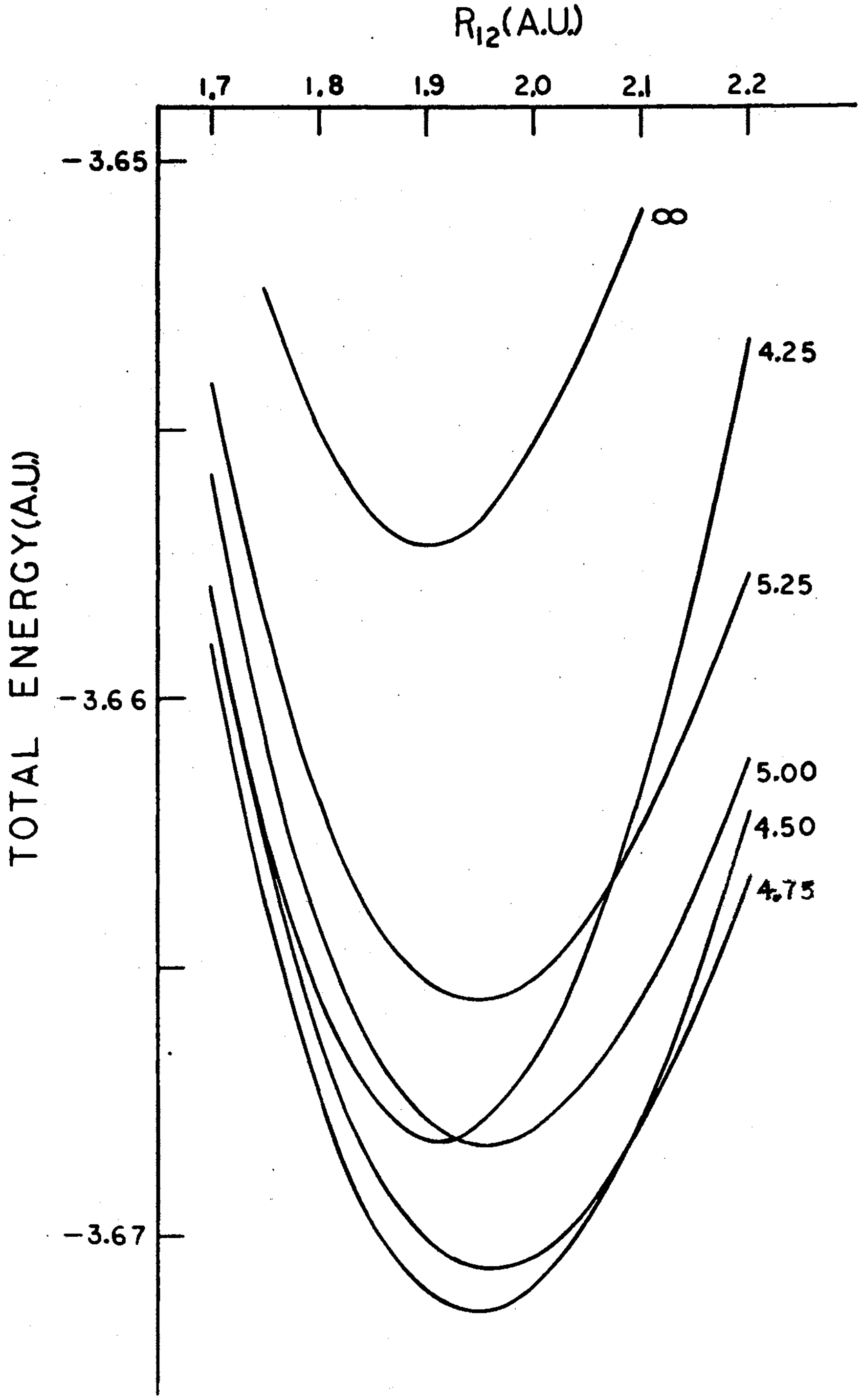

Figure 16. RDAO-1 SCF Energy vs. R_{12} for F-H••F

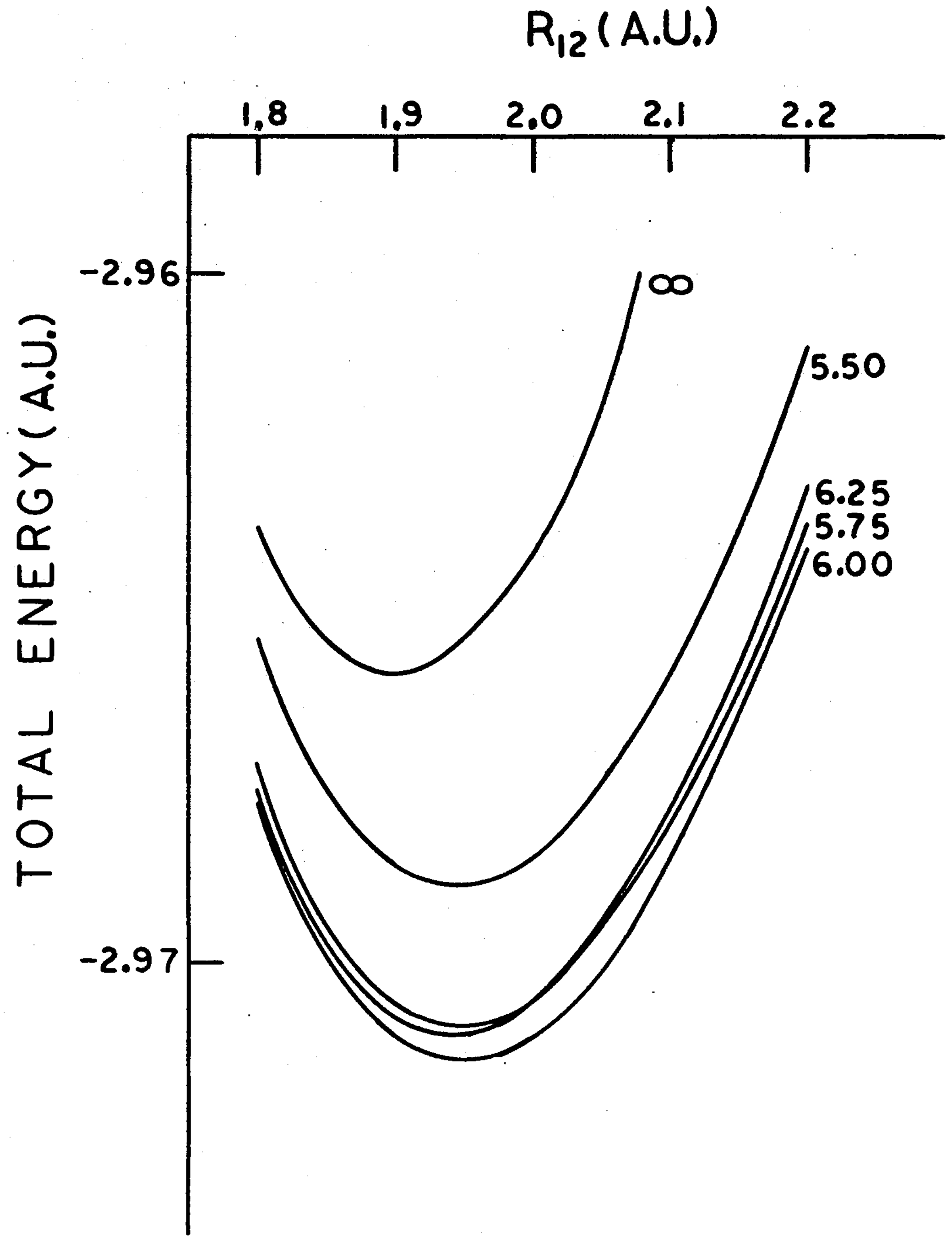

Figure 17. RDAO-1 SCF Energy vs. R_{12} for F-H∘∘S

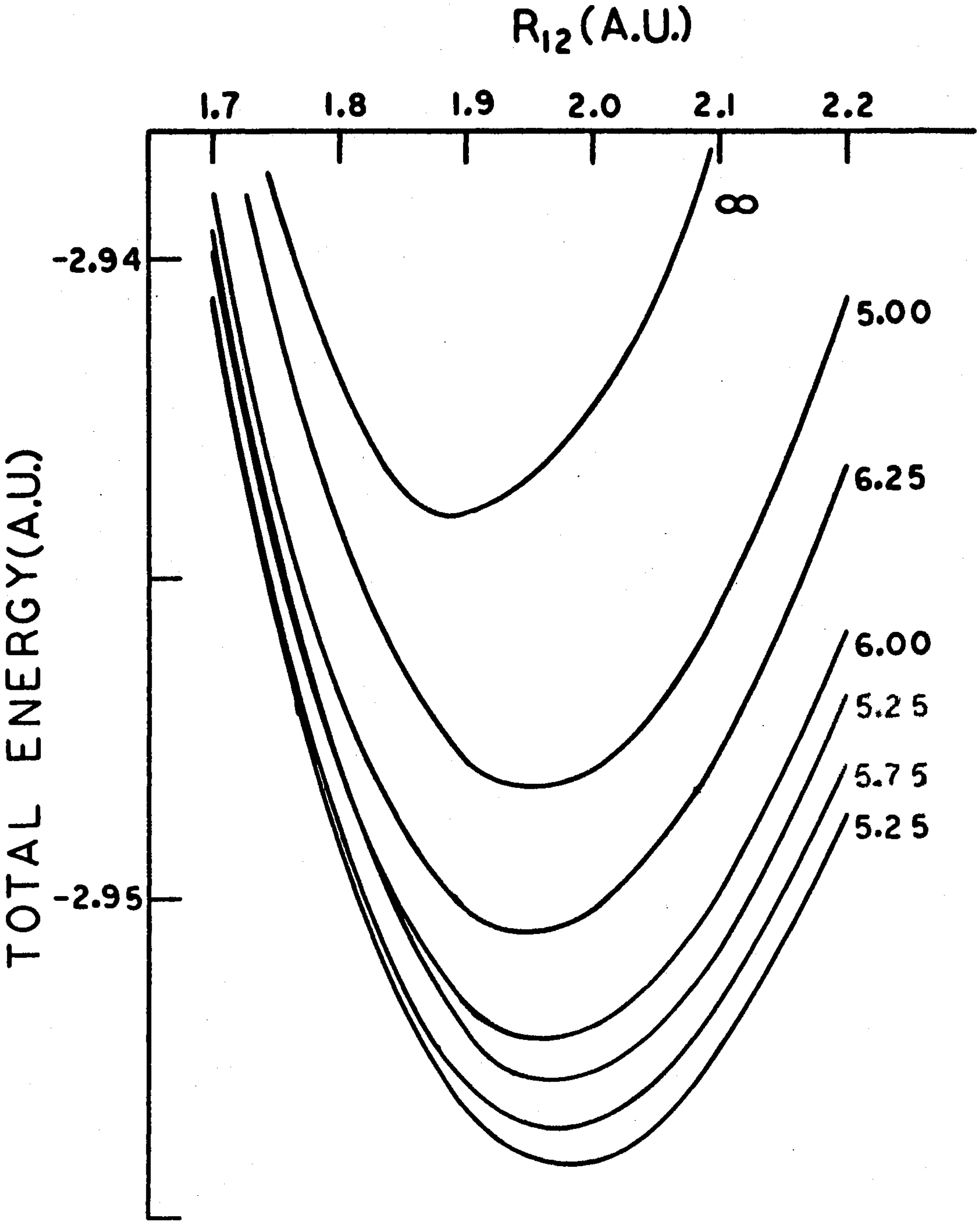

Figure 18. RDAO-1 SCF Energy vs. R_{12} for F-H··Cl

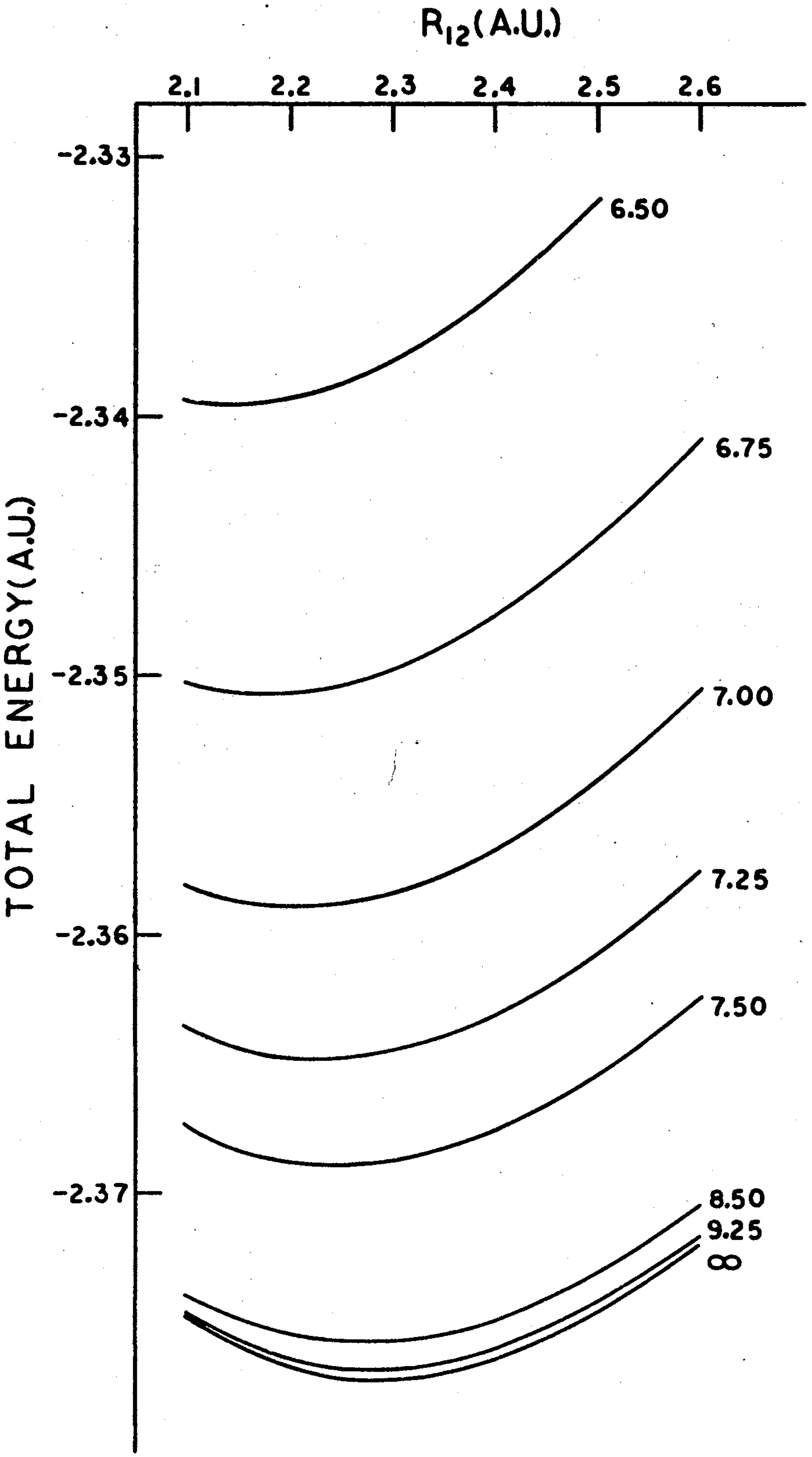

Figure 19. RDAO-1 SCF Energy vs. R_{12} for P-H••P

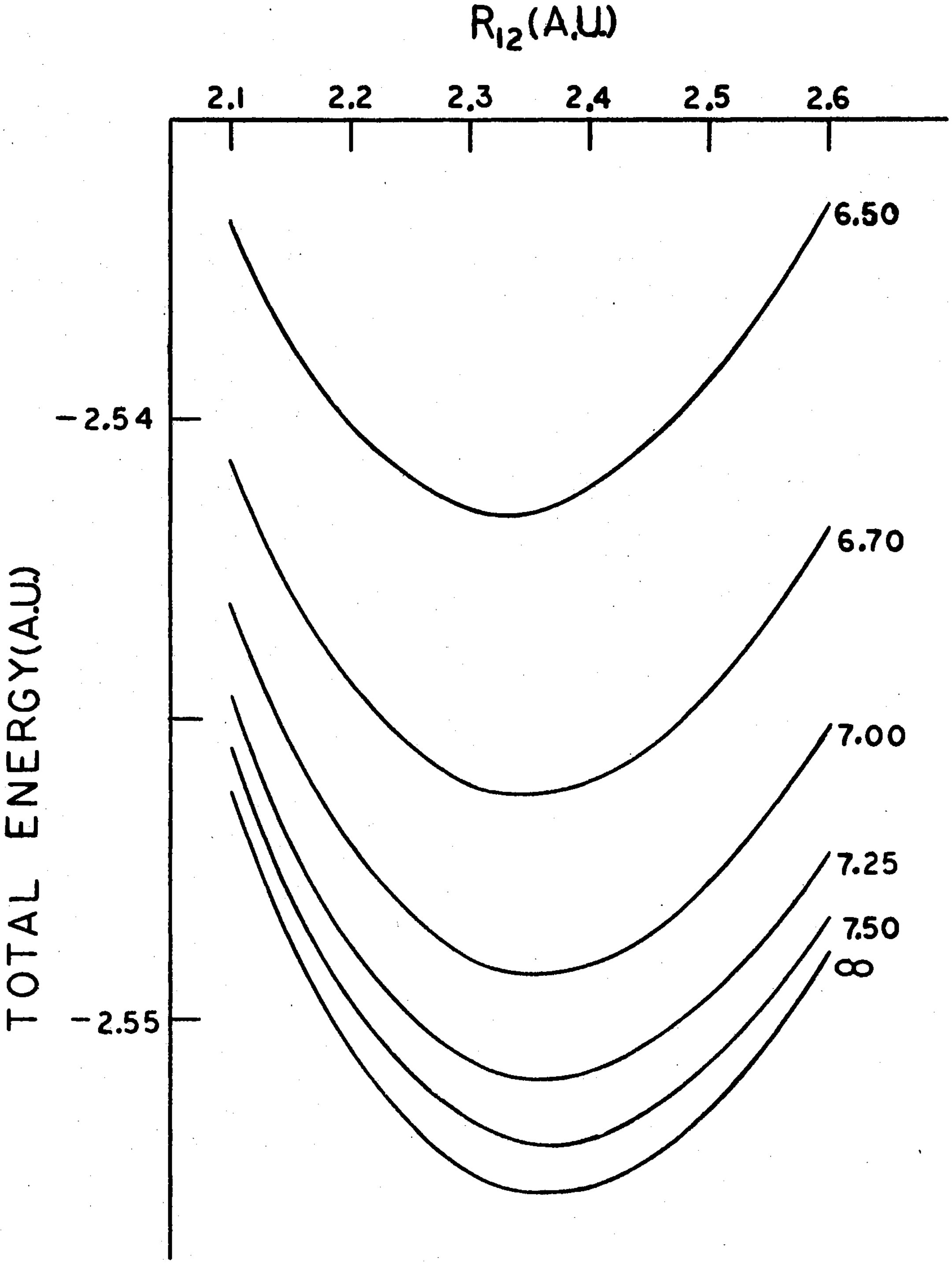

Figure 20. RDAO-1 SCF Energy vs. R_{12} for S-H··S

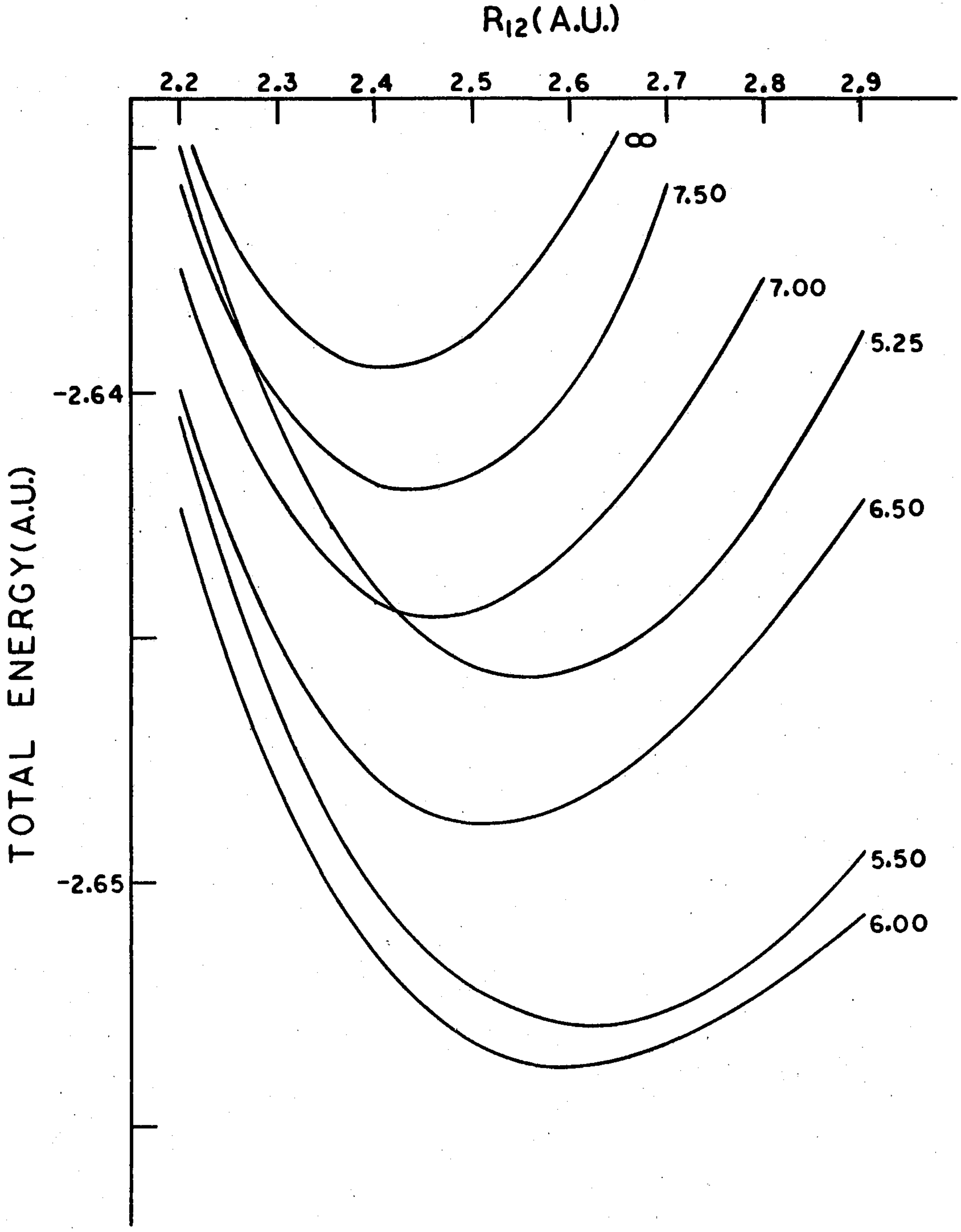

Figure-21. RDAO-1 SCF Energy vs. R_{12} for Cl-H··N

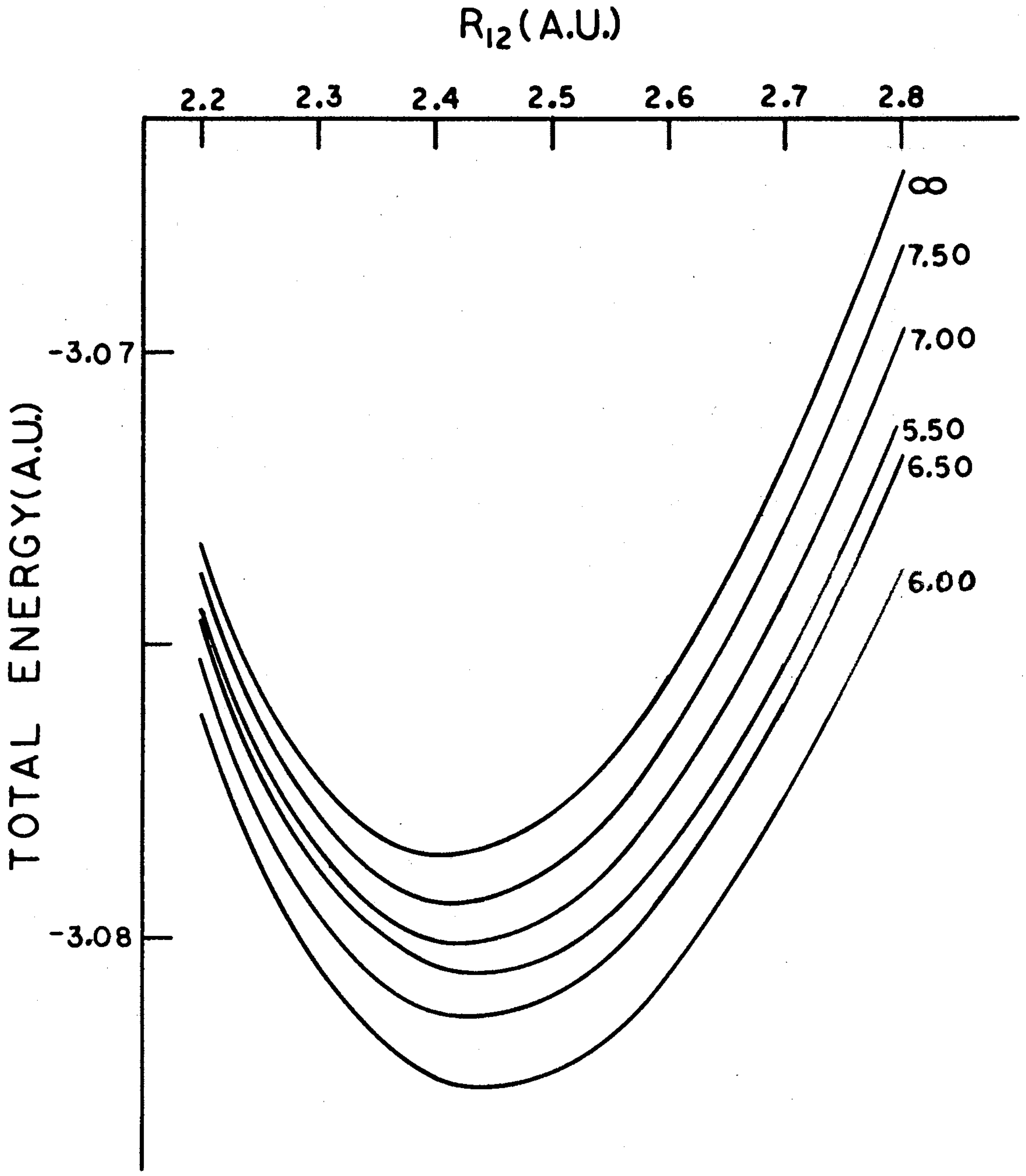

Figure 22. RDAO-1 SCF Energy vs. R_{12} for Cl-H∘∘O

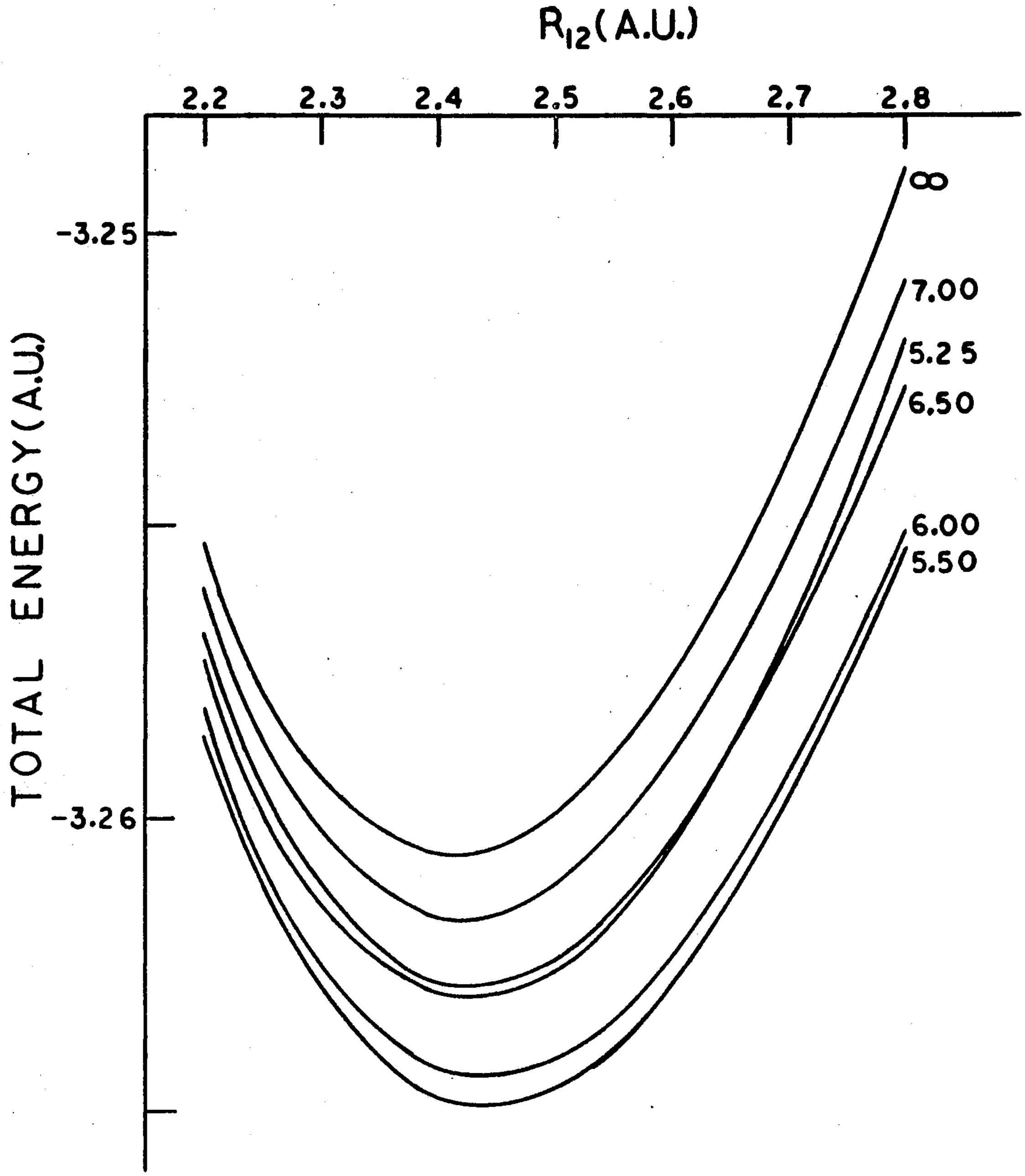

Figure 23. RDAO-1 SCF Energy vs. R_{12} for Cl-H∘∘F

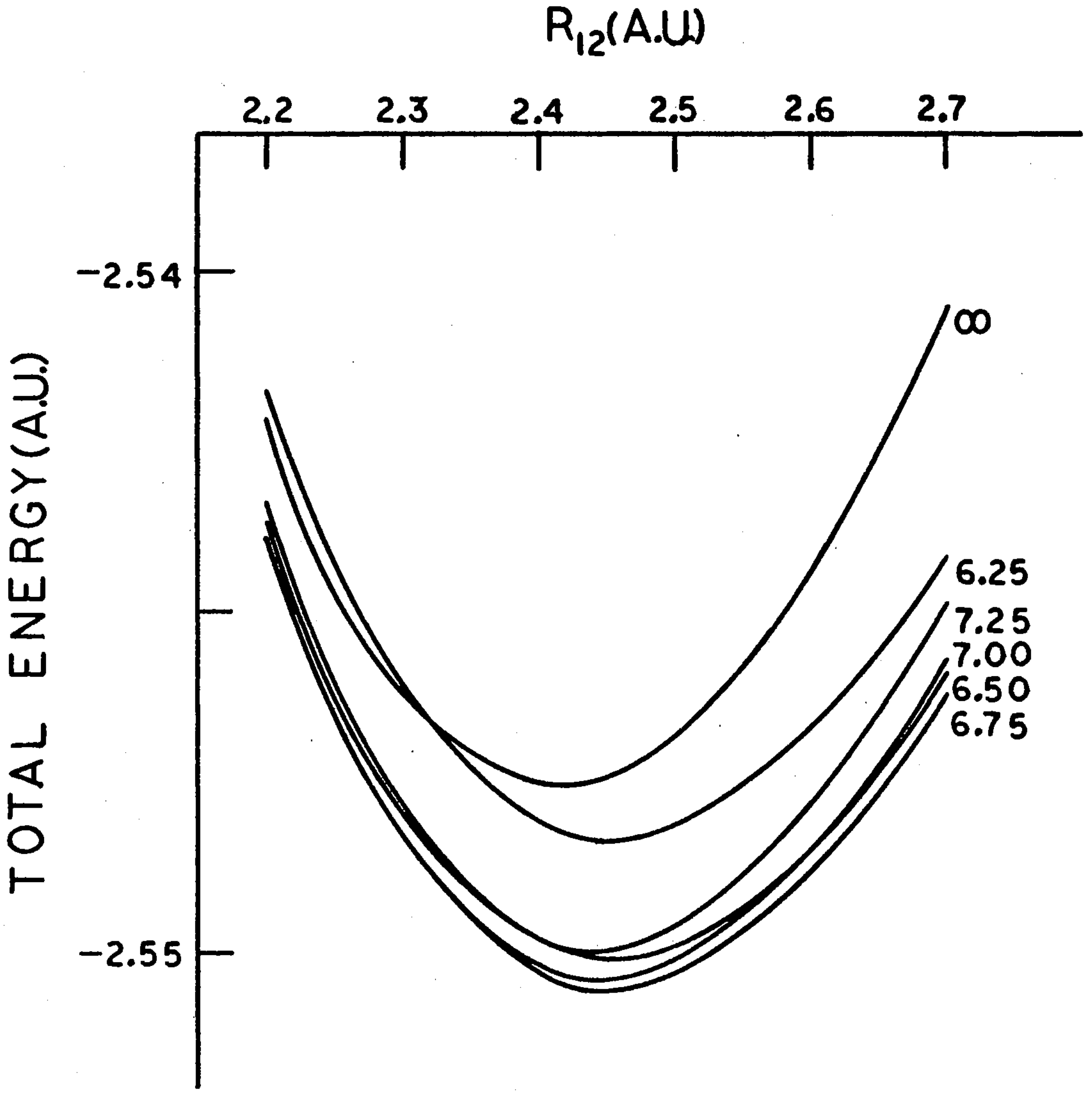

Figure 24. RDAO-1 SCF Energy vs. R_{12} for Cl-H··Cl

R_{13} for the X-H..X homologous series, Figure 27 the N-H··Y series, Figure 28 the O-H··Y series, Figure 29 the F-H··Y series, and Figure 30 the Cl-H··Y series. A separate graph, Figure 31, was used for the three systems O-H··N, F-H··N, and Cl-H··N as they displayed unexpectedly large energy differences.

The AO coefficients of the wave function for the calculational point closest to the equilibrium point for each system is listed in Table IV. Table V lists the calculated maximum energies of dissociation of X-H··Y into X-H+Y along with values from other calculations and some experimental values for comparison. Tables VI and VII give the equilibrium values obtained for R_{13} and R_{12} in each case along with values from experiment and other calculations with force constants for the X-H stretching vibration in Table VIII.

Discussion of Results

The X-H··X series is the one most readily discussed since more experimental data is available than for any of the other series. In particular, emphasis will be placed on the data from the hydrogen-bonded dimers $(NH_3)_2$, $(H_2O)_2$, $(FH)_2$, and $(H_2S)_2$ as these dimers would correspond most closely to the linear geometry and tetrahedral hybridization assumed in these calculations.

The binding energy curves of the X-H··X series exhibited in Figure 25 show deeper binding for shorter X··X separations falling in the order F>O>N>Cl as expected from the dimer data in Tables VI and VII. The maximum calculated dissociation energies are uniformly larger than the experimental energies with the associated X··X separations being smaller than experimental values. The most extreme energy difference

TABLE IV

SCF ATOMIC ORBITAL COEFFICIENTS

X-H Y	R_{12}	R_{13}	C_{11}	C_{12}	C_{13}	C_{21}	C_{22}	C_{23}
N-H••N	1.94	5.50	0.6546	0.3114	0.3886	-0.5030	0.0068	0.8824
N-H••O	2.00	5.00	0.1793	0.2289	0.8681	0.8052	0.2052	-0.4164
N-H••F	1.95	5.00	0.1140	0.1874	0.9238	0.8064	0.2364	-0.3125
N-H••S	1.90	7.25	0.7824	0.2948	0.0752	-0.1388	0.0188	0.9913
N-H••Cl	2.00	6.75	0.7572	0.3228	0.1233	-0.2029	0.2037	0.9813
O-H••N	2.14	4.75	0.4374	0.3286	0.6100	0.8055	-0.1151	-0.6240
O-H••O	1.90	5.00	0.3897	0.2005	0.7955	0.8108	0.0875	-0.5504
O-H••F	1.95	4.50	0.1352	0.1956	0.8991	0.8912	0.1361	-0.3110
O-H••S	1.90	6.25	0.8667	0.2035	0.0860	-0.2042	0.0670	0.9724
O-H••Cl	1.90	5.75	0.8568	0.2059	0.1237	-0.2638	0.0838	0.9570
F-H••N	2.15	4.50	0.3492	0.3456	0.6503	0.8632	0.0127	-0.5327
F-H••O	1.95	4.50	0.2217	0.2210	0.8463	0.8841	0.1205	-0.3988
F-H••F	1.95	4.50	0.1534	0.1951	0.8971	0.8924	0.1498	-0.3199
F-H••S	1.90	6.00	0.8653	0.2226	0.1030	-0.2333	0.0703	0.9620
F-H••Cl	2.00	5.25	0.7891	0.2525	0.2690	-0.4529	0.0741	0.8894
Cl-H••N	2.60	6.00	0.3486	0.3650	0.6714	0.7271	0.1129	-0.6580
Cl-H••O	2.40	6.00	0.1192	0.2030	0.9203	0.7597	0.2771	-0.3392
Cl-H••F	2.40	5.50	0.0608	0.1996	0.9311	0.7807	0.2718	-0.2887
Cl-H••Cl	2.40	6.75	0.6511	0.3477	0.3294	-0.4081	-0.0219	0.9220

TABLE V

RDAO-1 SCF MAXIMUM BINDING ENERGIES

X-H··Y	Calculated Maximum Binding Energy (kcal/mole)	Experimental Energy Ranges	Experimental Dimer Energies	Other Works
N-H··N	5.4	3.0 - 5.0[d] 1.7 - 5.2[e]	4.5[a]	3.69[c], 4.06[b]
N-H··O	3.5	1.9 - 7.3[e]		1.26[c]
N-H··F	4.0			1.5[c]
N-H··S	0.4	1.1 - 5.6[e]		
N-H··Cl	0.9			
O-H··N	24.5	1.7 - 9.1[e]		10.51[c]
O-H··O	6.9	3.0 - 6.0[d] 1.7 - 8.0[e]	5.0[d]	5.94[c], 6.31[b]
O-H··F	10.0	1.0 - 9.0[e]		3.38[c]
O-H··S	2.4	3.3 - 5.1[e]		
O-H··Cl	4.5	1.0 - 9.0[e]		
F-H··N	28.5			13.08[c]
F-H··O	11.6			10.07[e]
F-H··F	8.9	5.0 - 7.0[f]	6.8[d]	6.58[c], 6.92[b]
F-H··S	3.5			
F-H··Cl	6.9			
Cl-H··N	10.2			
Cl-H··O	2.5			
Cl-H··F	2.7			
Cl-H··Cl	1.9			

a. Reference 89
b. Reference 60
c. Reference 63
d. Reference 27
e. Reference 90
f. Reference 91

TABLE VI

RDAO-1 SCF EQUILIBRIUM SEPARATION

X-H··Y	Calculated Equilibrium R_{13} (a.u.)	Experimental Average (a.u.)	Experimental Dimer R_{13}	Other Work
N-H··N	5.50	5.86[a]	6.39[a]	5.24[c], 5.33[d]
N-H··O	5.03	5.58[a]		5.35[d]
N-H··F	4.90	5.25[a]		5.20[d]
N-H··S	7.73	6.43[b]		
N-H··Cl	6.75	6.07[a]		
O-H··N	4.68	5.29[a]		4.99[d]
O-H··O	4.83	5.09[a]	5.22[a]	4.80[c], 4.78[d]
O-H··F	4.50			4.82[d]
O-H··S	6.25	6.20[b]		
O-H··Cl	5.75	5.82[a]		
F-H··N	4.55			4.67[d]
F-H··O	4.57			4.56[d]
F-H··F	4.55	4.61[a]	4.82[a]	4.59[c], 4.57[d]
F-H··S	6.05			
F-H··Cl	5.50			
Cl-H··N	5.75			
Cl-H··O	5.95			
Cl-H··F	5.65			
Cl-H··Cl	6.76			

[a] Reference 27

[b] Reference 93

[c] Reference 60

[d] Reference 63

TABLE VII

RDAO-1 SCF X-H BOND LENGTHS

X-H··Y	Calculated Equilibrium R_{12} (a.u.) No H-Bond	Experimental R_{12} (a.u.) No H-Bond	Equilibrium R_{12} (a.u.) H-Bond	Experimental R_{12} (a.u.) H-Bond
N-H··N	1.94	1.91[a]	2.02	1.92[b]
N-H··O	1.94		1.94	1.96 - 2.04[b]
N-H··F	1.94		1.95	1.94[b]
N-H··S	1.94		1.94	
N-H··Cl	1.94		1.95	1.94[b]
O-H··N	1.87	1.81[a]	2.15	
O-H··O	1.87		1.94	1.91
O-H··F	1.87		1.93	
O-H··S	1.87		1.91	
O-H··Cl	1.87		1.94	
F-H··N	1.90	1.73[a]	2.12	
F-H··O	1.90		1.96	
F-H··F	1.90		1.96	1.89[a]
F-H··S	1.90		1.95	
F-H··Cl	1.90		1.98	
Cl-H··N	2.41	2.41[a]	2.59	
Cl-H··O	2.41		2.44	
Cl-H··F	2.40		2.44	
Cl-H··Cl	2.42		2.45	

a. Reference 92
b. Reference 27, Tables 9-IV and 9-V

TABLE VIII

RDAO-1 SCF FORCE CONSTANTS AND RATIOS

X-H••Y	Calculated Force Constant k_{X-H} (10^5 dyne/cm) No H-Bond	Experimental Force Constant (10^5 dyne/cm) No H-Bond	Calculated Force Constant $k_{X-H \cdot\cdot Y}$ (10^5 dyne/cm) H-Bond	Ration of $\frac{k_{X-H \cdot\cdot Y}}{k_{X-H}}$
N-H••N	3.73	6.1[a]	2.33	.62
N-H••O	3.88		3.65	.94
N-H••F	3.88		3.57	.92
N-H••S	3.42		3.11	.91
N-H••Cl	3.58		3.42	.96
O-H••N	4.66	7.7[a]	2.49	.53
O-H••O	4.28		3.89	.91
O-H••F	4.35		4.04	.93
O-H••S	4.13		3.81	.92
O-H••Cl	4.35		3.73	.86
F-H••N	6.22	9.65[a]	2.80	.45
F-H••O	6.22		5.29	.85
F-H••F	6.22		5.13	.82
F-H••S	5.91		4.35	.74
F-H••Cl	5.91		4.19	.71
Cl-H••N	2.95	5.16[a]	1.71	.58
Cl-H••O	3.11		2.80	.90
Cl-H••F	3.11		2.80	.90
Cl-H••Cl	3.27		3.11	.95

a. Calculated from data in Reference 95

was 2.1 kcal/mole for the F-H••F system. The equilibrium X••X separations are within 10% of the experimental values for O and F and within 15% for N. No binding at all was obtained for S-H••S and P-H••P with the SCF wavefunction but this was corrected by using the split shell function as discussed later.

The other series X-H••Y for the most part show greater binding at shorter X••Y equilibrium separations in the order Y = F > O > Cl > S for X being N, O, F, or Cl. These series are shown in Figures 25-30. The experimental ranges of energies taken from Murthy and Rao do not really admit any detailed comparisons since they overlap to a very large extent and each range is for a wide variety of compounds.

The binding energy curves of the X-H••N series (Figure 30) for X = O, F, Cl give maximum dissociation energies much larger than would seem to be reasonable. Comparison with Kollman and Allen's CNDO mixed dimer calculations also is unfavorable, the RDAO-1 values for the binding energies being over twice as large as the CNDO values for the O-H••N and F-H••N systems. There is, however, qualitative agreement with Kollman and Allen's results in that the system O-H••N is predicted to have much stronger bonding than the N-H••O system and to be more strongly bound than the O-H••O system.

Table VI lists the equilibrium X••Y separations for all the systems considered. Also included are averages of experimental values, the experimental values for the dimers and values obtained by Hoyland and Kier and Kollman and Allen from CNDO calculations. All of the experimental averages are from Table 9 - XXVI of Pimentel and McClellen except for the N-H••S and O-H••S systems which are given by Strinivasan and Chacko (93).

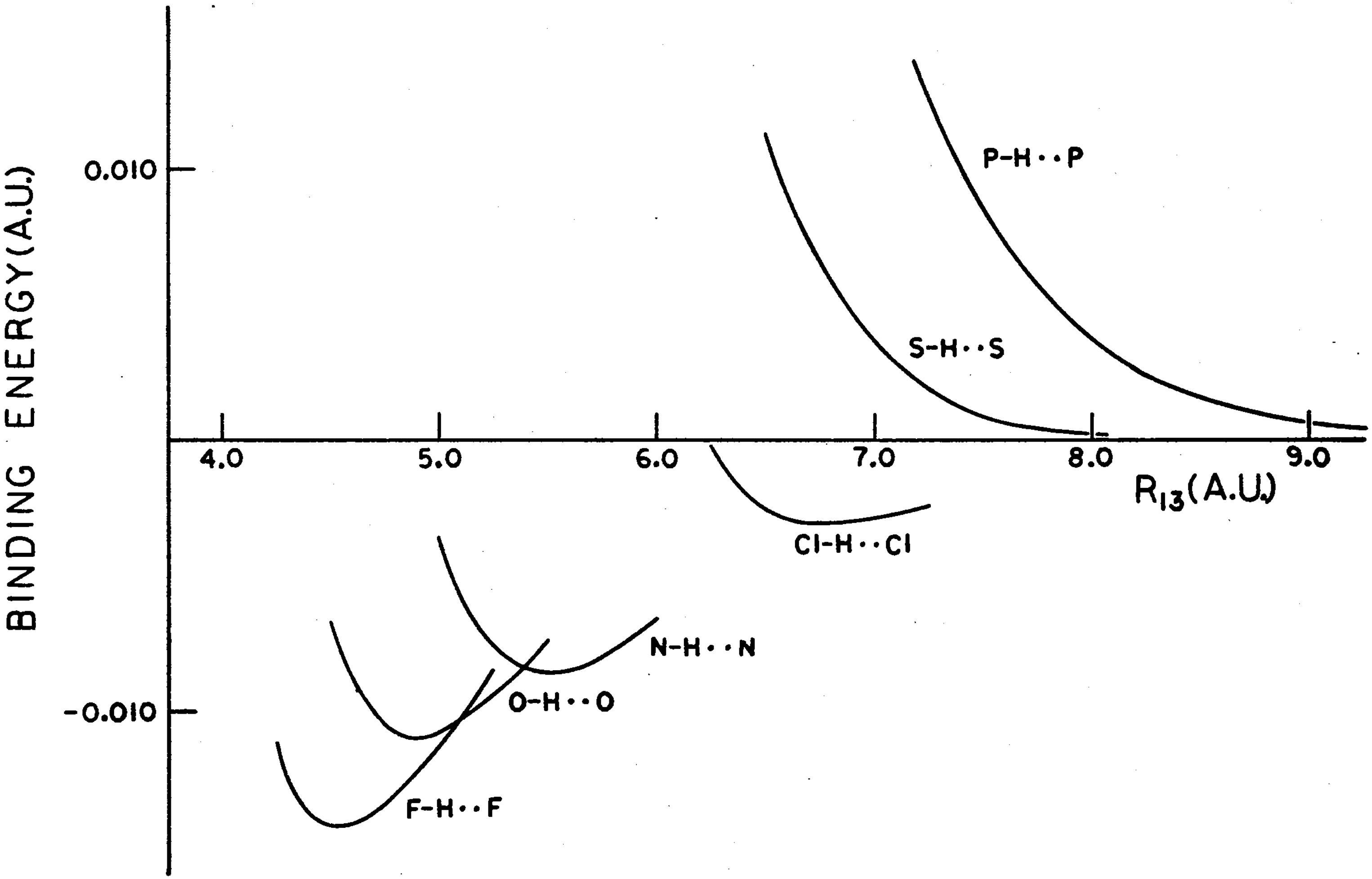

Figure 25. RDAO-1 SCF Binding Energies vs. R_{13} for X-H··X Systems

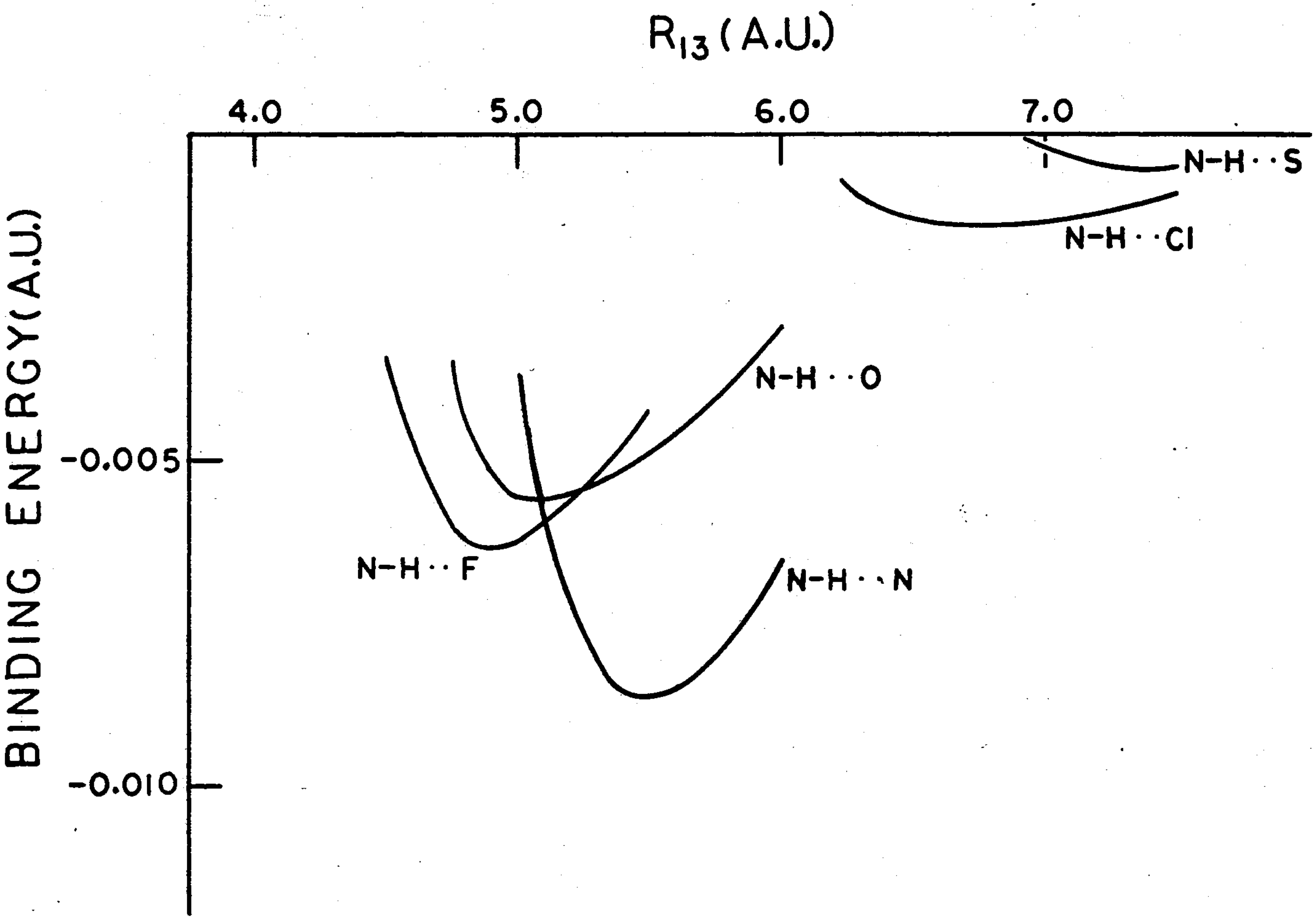

Figure 26. RDAO-1 SCF Binding Energies vs. R_{13} for N-H··Y Systems

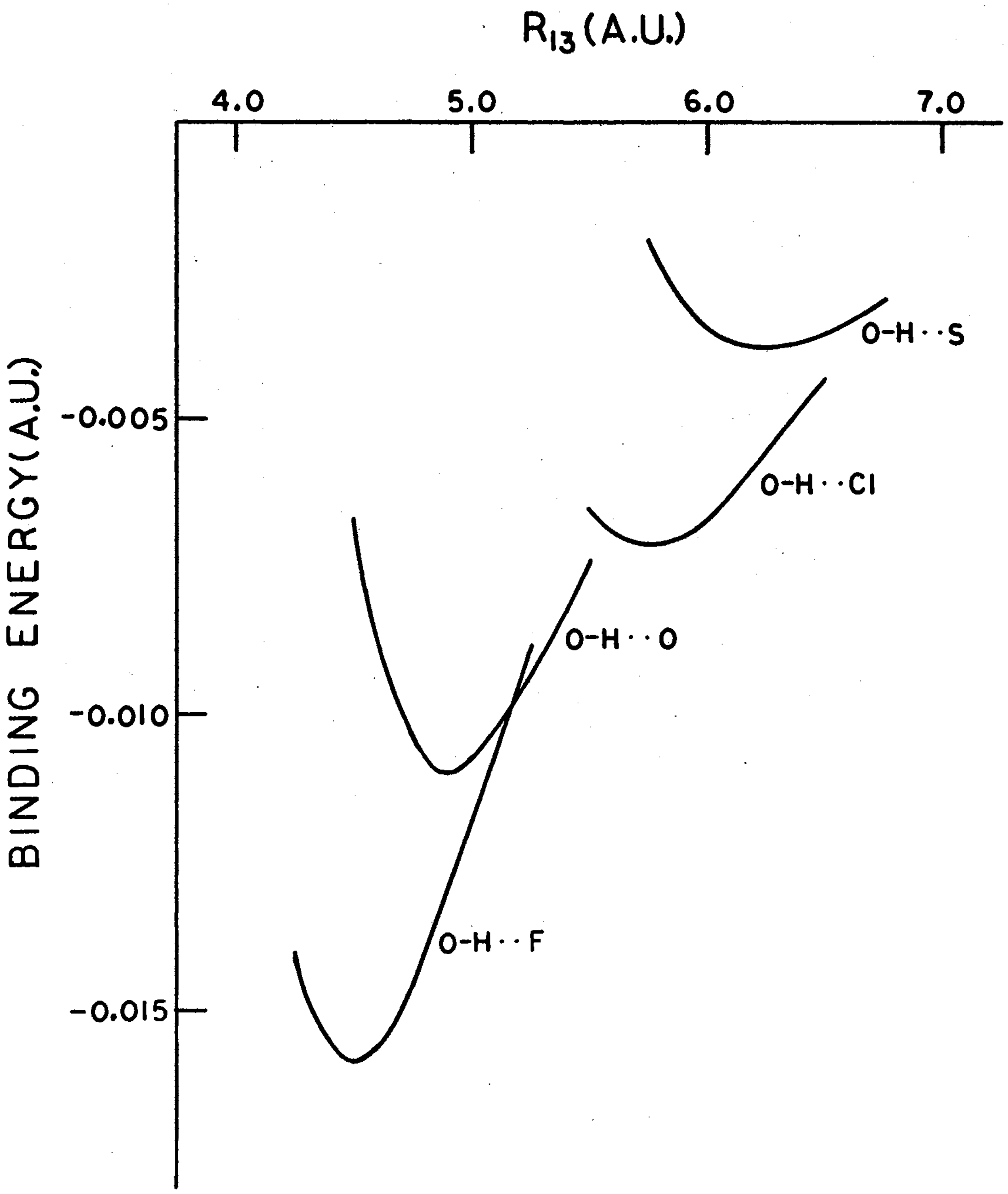

Figure 27. RDAO-1 SCF Binding Energies vs. R_{13} for O-H··Y Systems

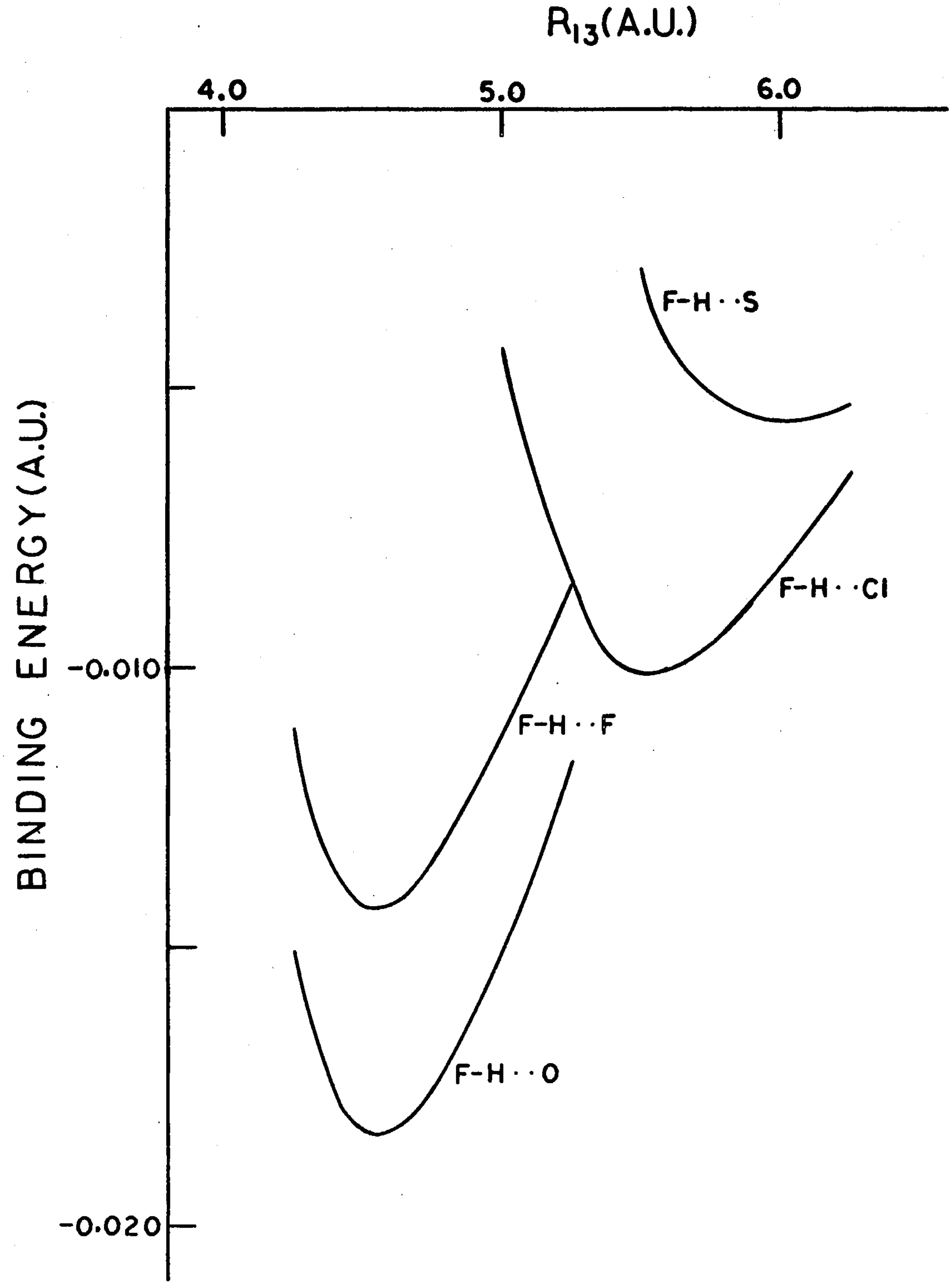

Figure 28. RDAO-1 SCF Binding Energies vs. R_{13} for F-H··Y Systems

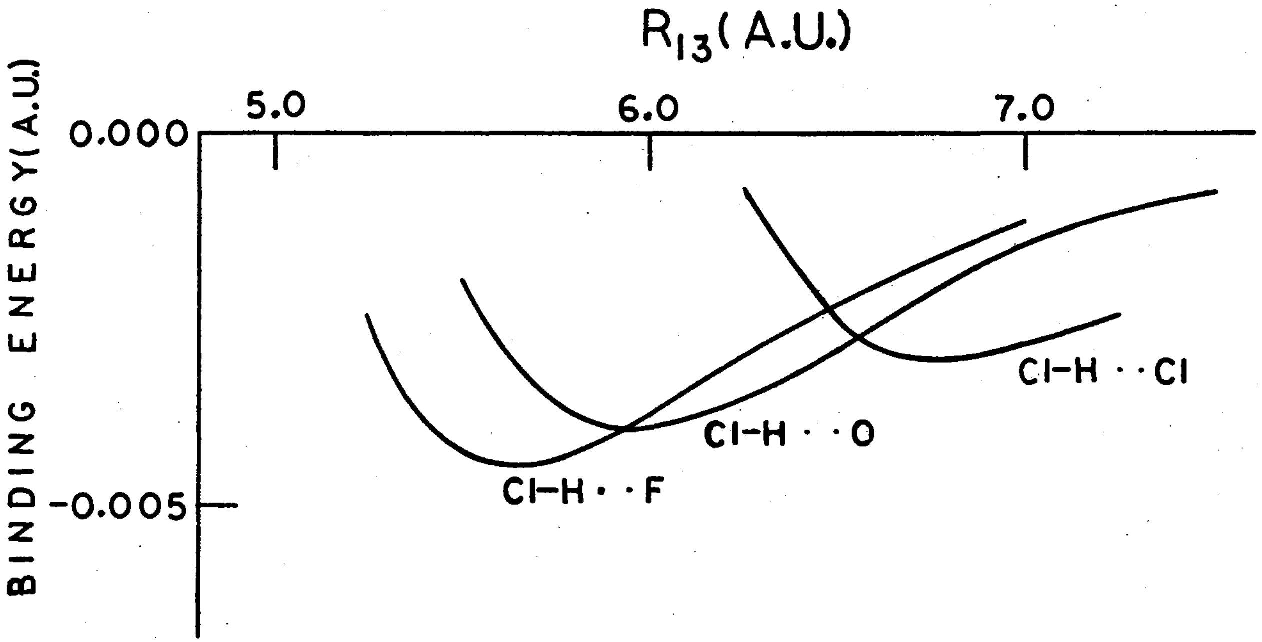

Figure 29. RDAO-1 SCF Binding Energies vs. R_{13} for Cl-H..Y Systems

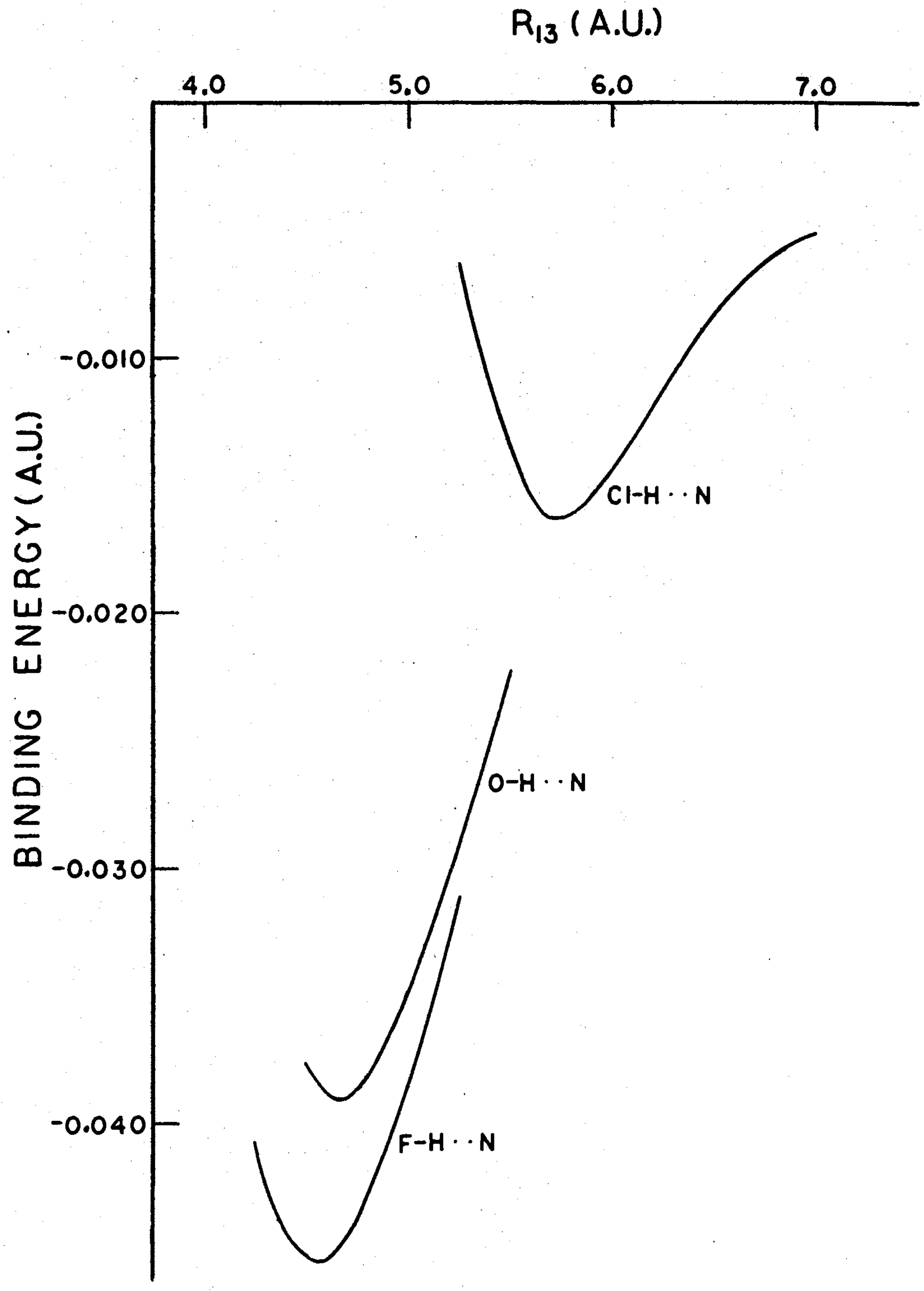

Figure 30. RDAO-1 SCF Binding Energies vs. R_{13} for X-H··N Systems

The equilibrium values of R_{13} are for the most part in good agreement with the experimental averages all being within ∿10% of these values except for the N-H··S and O-H··N systems. The N-H··S system has a length 20% longer than that predicted by the experimental average while the O-H··N system has a length 13% shorter. The N-H··Y sequence follows the experimental trends but the O··N and O··O separations are reversed in O-H··Y sequence. Again X··X distances follow the trend of the dimer data but are shorter.

In comparison with the CNDP values, the RDAO-1 values are almost the same for the O-H··O and F-H··F systems. There is a discrepency of 0.26 au for the N-H··N system in comparison with Kollman and Allen's value and 0.17 au with Hoyland and Kier's value, the RDAO-1 value being larger in both cases. It is to be noted also that the CNDO results order the lengths of the O-H··N and O-H··O systems and the lengths of the F-H··N and F-H··O systems opposite to the RDAO-1 order.

The X-H equilibrium are also in good agreement with experimental results both when hydrogen bonding is assumed and when the X-H system is isolated. Except for the case of F-H··X systems, the calculated are within 3% of experimental values. The F-H values are within 10% of experiment. Each system displays a stretching of the X-H distance when H-bonding is present, the X-H··N having the largest stretch in each series.

The decrease in the IR stretching frequency ν_s of the proton is a very prominent feature of hydrogen bonding. Pimentel and McClellen state that the decrease $\Delta\nu_s$ is of the order of 10% in many systems. This means that the corresponding force constants k would be decreased by about 20%. The force constants for the vibrational mode of the proton are given in Table VIII along with the ratio $k_{X-H..Y}/k_{X-H}$.

The force constants for case of no hydrogen bonding are all within 50% of the values calculated from the diatomic data contained in the book by Herzberg and are sequenced in the experimental order $F > O > N > Cl$.

The ratios of force constants clearly illustrates the decrease of the stretching frequency as each ratio is less than unity. This is in contrast to the results of Kollman and Allen whose CNDO results predicted a slight increase for the HF dimer. The most marked predicted decreases by the RDAO-1 method is for the X-H··N series where the ratios range from 0.45 to 0.62 in the order $F < O < Cl < N$.

CHAPTER IV

RDAO-1 SPLIT SHELL CALCULATIONS AND RESULTS

A program to perform the split shell calculationsusing the formulation derived in Chapter II was written for the IBM 360/50 and 360/65 computers in the Fortran IV language. As in the closed shell case the AO overlap subroutine, and the subroutines CIEG and GIVENS employed double precision arithmetic. The input parameters used for integral evaluations are given in Table II. The program took about 34 seconds to complete a calculation for a single point on the IBM 360/50 and about 9 seconds for the IBM 360/65.

As was done for the closed shell calculation, the total energy for the O-H··O system was calculated over an extended range of R_{12} for an O··O separation of 5.00 au. The resulting energy vs. R_{12} is given in Figure 31 and the wavefunction coefficients in Table IX.

The results for this extended range calculation reflect the anamolous behavior found in the corresponding SCF calculation in Chapter III. A local minimum in the total energy is found near the experimental value of the O-H distance but showing a flattening at $R_{12} \simeq 1.25$ au and sudden decrease at $R_{12} \simeq 3.50$ au. Again, the coefficients of the four VB functions which are most important at 2.0 au, namely b_2, b_4, b_7, and b_{12} show a sudden and very drastic decrease in absolute magnitude in the region 3.25-3.50 au. The coefficients b_{16} and b_{18} show an equally dramatic increase in the same region but are small at

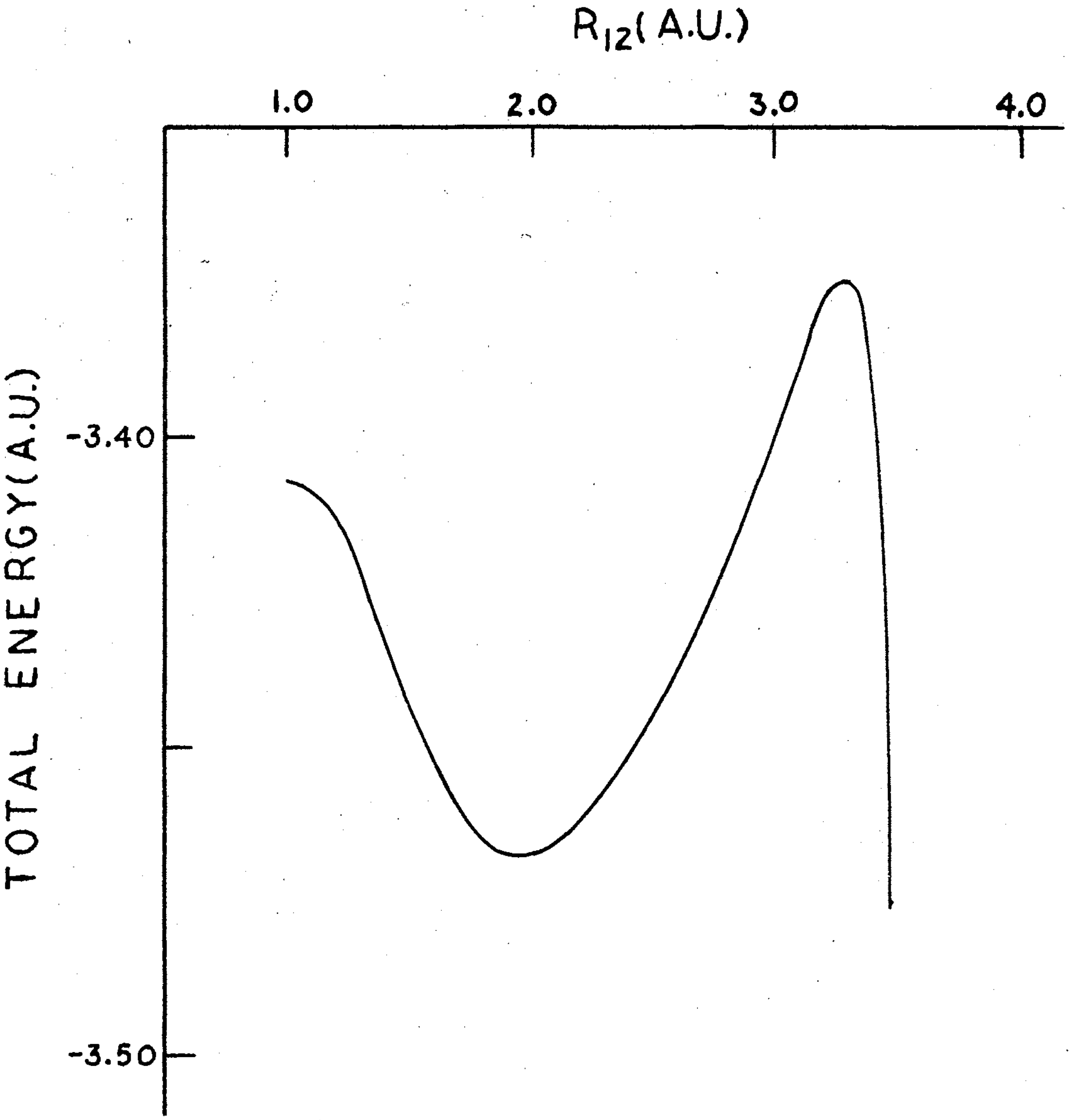

Figure 31. RDAO-1 Split Shell Total Energy vs. R_{12} for O-H··O for Extended Range of R_{12}

TABLE IX

SPLIT SHELL WAVEFUNCTION AND TOTAL ENERGY

R_{12}	1.00	1.25	1.50	1.75	2.00	2.25	2.50	2.75	3.00	3.25	3.50	3.75	4.00
E	-3.4076	-3.4165	-3.4430	-3.4636	-3.4681	-3.4603	-3.4449	-3.4242	-3.3990	-3.3764	-3.7174	-4.5895	-6.1440
b_1	-0.0010	-0.0010	-0.0011	0.0013	0.0057	0.0134	0.0259	-0.0460	-0.0778	-0.1130	-0.0079	-0.0016	-0.0067
b_2	-0.0208	0.0536	0.1187	0.1735	0.2260	0.2777	0.3252	-0.3601	-0.3676	-0.2959	0.0056	-0.0002	0.0050
b_3	0.0015	0.0053	0.0074	0.0082	0.0084	0.0083	0.0078	-0.0071	-0.0060	-0.0055	0.0164	-0.0040	0.0089
b_4	1.6843	1.3235	0.9985	0.8100	0.7129	0.6618	0.6321	-0.6107	-0.5876	-0.5078	0.0086	-0.0002	-0.0009
b_5	0.1323	0.0929	0.0585	0.0384	0.0293	0.0269	0.0279	-0.0298	-0.0294	-0.0164	-0.0063	-0.0010	-0.0036
b_6	-0.0000	-0.0007	-0.0010	-0.0010	-0.0008	-0.0004	-0.0001	-0.0001	0.0000	0.0010	-0.0047	0.0014	-0.0028
b_7	-0.0144	-0.0211	-0.0457	-0.0731	-0.1014	-0.1291	-0.1530	0.1697	0.1782	0.1650	-0.0019	-0.0001	-0.0077
b_8	-0.0021	0.0023	0.0024	0.0028	0.0039	-0.0066	0.0127	-0.0271	-0.0681	-0.2814	0.1527	0.0760	0.2226
b_9	0.2458	0.1092	0.0425	0.0145	0.0043	0.0009	-0.0003	0.0009	0.0013	0.0018	0.0000	0.0000	-0.0020
b_{10}	-0.0524	-0.0407	-0.0350	-0.0259	-0.0175	-0.0107	-0.0056	0.0029	0.0037	0.0137	0.0315	0.0061	0.1189
b_{11}	0.0022	0.0002	0.0005	0.0004	0.0005	0.0008	0.0012	-0.0023	-0.0072	-0.1034	1.0501	-1.4478	-1.7282
b_{12}	-1.2829	-0.5861	-0.0556	0.2284	0.3638	0.4173	0.4197	-0.3866	-0.3296	-0.2376	0.0023	0.0000	-0.0031
b_{13}	0.1278	0.0105	-0.0336	-0.0425	-0.0396	-0.0319	-0.0217	0.0096	-0.0065	-0.0560	0.0207	0.0091	0.0328
b_{14}	-0.0500	-0.0044	0.0022	-0.0050	-0.0131	-0.0188	-0.0213	0.0210	0.0183	0.0122	0.0047	0.0026	0.0463
b_{15}	0.0025	0.0002	0.0004	0.0007	0.0005	0.0001	-0.0005	0.0013	0.0002	0.0027	0.0376	-0.1245	-0.2627
b_{16}	0.0024	0.0032	0.0025	0.0027	0.0029	0.0031	0.0034	-0.0043	-0.0077	-0.0584	0.2644	-0.0081	0.1362
b_{17}	-0.0048	-0.0012	0.0009	0.0020	0.0028	0.0036	0.0042	-0.0045	-0.0049	-0.0129	0.0025	-0.0075	-0.0539
b_{18}	0.0008	0.0013	0.0017	0.0017	0.0015	0.0010	0.0004	0.0003	0.0008	0.0629	-0.2981	0.8243	1.3465
b_{19}	-0.0038	-0.0016	-0.0015	-0.0013	0.0001	0.0041	0.0116	-0.0242	-0.0457	-0.0993	0.0222	-0.0315	-0.0900
b_{20}	-0.0297	-0.0213	-0.0164	-0.0156	-0.0162	-0.0180	-0.0224	0.0318	0.0513	0.1081	-0.0212	0.0314	0.0810

around 2.0 au. On the other side of the equilibrium region b_4 and b_{12} show marked decreases in absolute magnitude when the O-H separation is increased from 1.0 au to 1.25 au. Similar split shell calculations for O-H··N, N-H··O, and N-H··N for R_{13} taken to be 5.25 au, 5.25 au and 5.50 au respectively gave qualitatively the same behavior.

In view of this behavior of energy and wave function at both large and small X-H separations, attention was confined to the region around experimental R_{12} values as in the SCF calculations.

RDAO-1 Split Shell Results

Calculations were performed on the X-H··X systems where X was taken to be N, O, F, P, S and Cl. The parameters used for the integral evaluations were the same as for the closed shell calculations and are listed in Table II. As with the SCF closed shell computations, the potential energy for the motion of the proton around the equilibrium separation was calculated for several finite X··X separations and for an infinite separation. The resulting energy curves for each X-H··X system are shown in Figures 32-37. The binding energies as functions of the X··X separations are shown in Figure 38 with the equilibrium values of the binding energy, R_{12}, R_{13} and the force constants derived from the energy curves given in Table X. The coefficients for the wave functions at the X-H··X configuration computational point closest to the equilibrium configuration is given in Table XI.

Figures 32-37 clearly predict that hydrogen bonding takes place for all the X-H··X systems with a lengthening of the X-H separation for X = N, O, F, and Cl. A broadening of the energy curves is observed for values of R_{13} near the equilibrium value for all the systems.

TABLE X

RDAO-1 SPLIT SHELL RESULTS

X-H··X	N-H··N	O-H··O	F-H··F	P-H··P	S-H··S	Cl-H··Cl
Calculated - E(kcal/mole)	7.2	7.7	9.9	0.6	1.2	2.5
Experimental - E(kcal/mole)	4.5[a]	5.0[b]	6.8[b]	---	1.7[c]	---
Calculated R_{13} (a.u.)	5.40	4.87	4.54	9.00	7.87	6.68
Experimental R_{13} (a.u.)	6.39[b]	5.22[b]	4.82[b]	---	7.28[f]	---
Calculated R_{12}(a.u.), No H-Bond	1.95	1.90	1.92	2.44	2.44	2.46
Experimental R_{12}(a.u.), No H-Bond	1.91[d]	1.81[d]	1.73[d]	2.68[d]	2.50[d]	2.41[d]
Calculated R_{12}(a.u.), H-Bond	2.04	1.95	1.96	2.38	2.42	2.48
Experimental R_{12}(a.u.), H-Bond	1.92[b]	1.91[d]	1.89[d]	---	---	---
Calculated Force Constant (10^5dyne/cm) No H-Bond	3.8	4.4	4.7	0.8	1.7	2.5
Experimental Force Constant (10^5dyne/cm) No H-Bond	6.1[e]	7.7[e]	9.7[e]	---	4.14[g]	5.2[e]
Calculated Force Constant (10^5dyne/cm) H-Bond	1.7	3.0	3.8	---	1.6	2.1
Ratio of Force Constants	0.61	0.68	0.81	---	0.94	0.84

a. Reference 89
b. Reference 27
c. Reference 96
d. Reference 92
e. Calculated from data in Reference 95
f. Reference 94
g. Reference 62

TABLE XI

RDAO-1 SPLIT SHELL COEFFICIENTS

X-H••Y	N-H••N	O-H••O	F-H••F	P-H••P	S-H••S	Cl-H••Cl
R_{12}	2.00	1.90	2.00	2.40	2.40	2.50
R_{13}	5.50	4.75	4.50	9.00	8.00	6.75
b_1	0.0099	0.0062	0.0120	-0.0006	-0.0074	0.0048
b_2	0.2328	0.2259	0.2499	-0.0662	-0.1031	0.2238
b_3	0.0109	0.0083	0.0055	-0.0055	-0.0095	0.0187
b_4	0.5901	0.7431	0.7083	-0.3804	-0.5230	0.5473
b_5	0.0236	0.0371	0.0191	-0.0711	-0.0823	0.0765
b_6	-0.0026	-0.0005	-0.0004	-0.0036	-0.0030	0.0021
b_7	-0.1397	-0.1027	-0.1212	0.0290	-0.0398	-0.1009
b_8	0.0098	0.0051	0.0078	0.0022	0.0029	-0.0038
b_9	0.0590	0.0371	0.0098	-0.1149	-0.0936	0.0689
b_{10}	-0.0681	-0.0195	-0.0146	0.0257	0.0196	-0.0189
b_{11}	0.0072	0.0010	0.0013	-0.0000	-0.0001	0.0013
b_{12}	0.4220	0.2954	0.3631	-0.6477	-0.5506	0.5450
b_{13}	-0.0236	-0.0392	-0.0280	0.0338	0.0649	-0.0698
b_{14}	-0.0034	-0.0089	-0.0105	0.0312	0.0426	-0.0330
b_{15}	0.0009	0.0006	0.0003	-0.0007	-0.0023	0.0024
b_{16}	0.0055	0.0026	0.0025	-0.0077	0.0053	-0.0011
b_{17}	0.0032	0.0026	0.0025	-0.0048	-0.0079	0.0084
b_{18}	0.0099	0.0017	0.0015	-0.0021	-0.0028	0.0044
b_{19}	0.0043	0.0011	0.0047	0.0027	0.0067	-0.0089
b_{20}	-0.0278	-0.0155	-0.0194	-0.0085	-0.0131	-0.0107

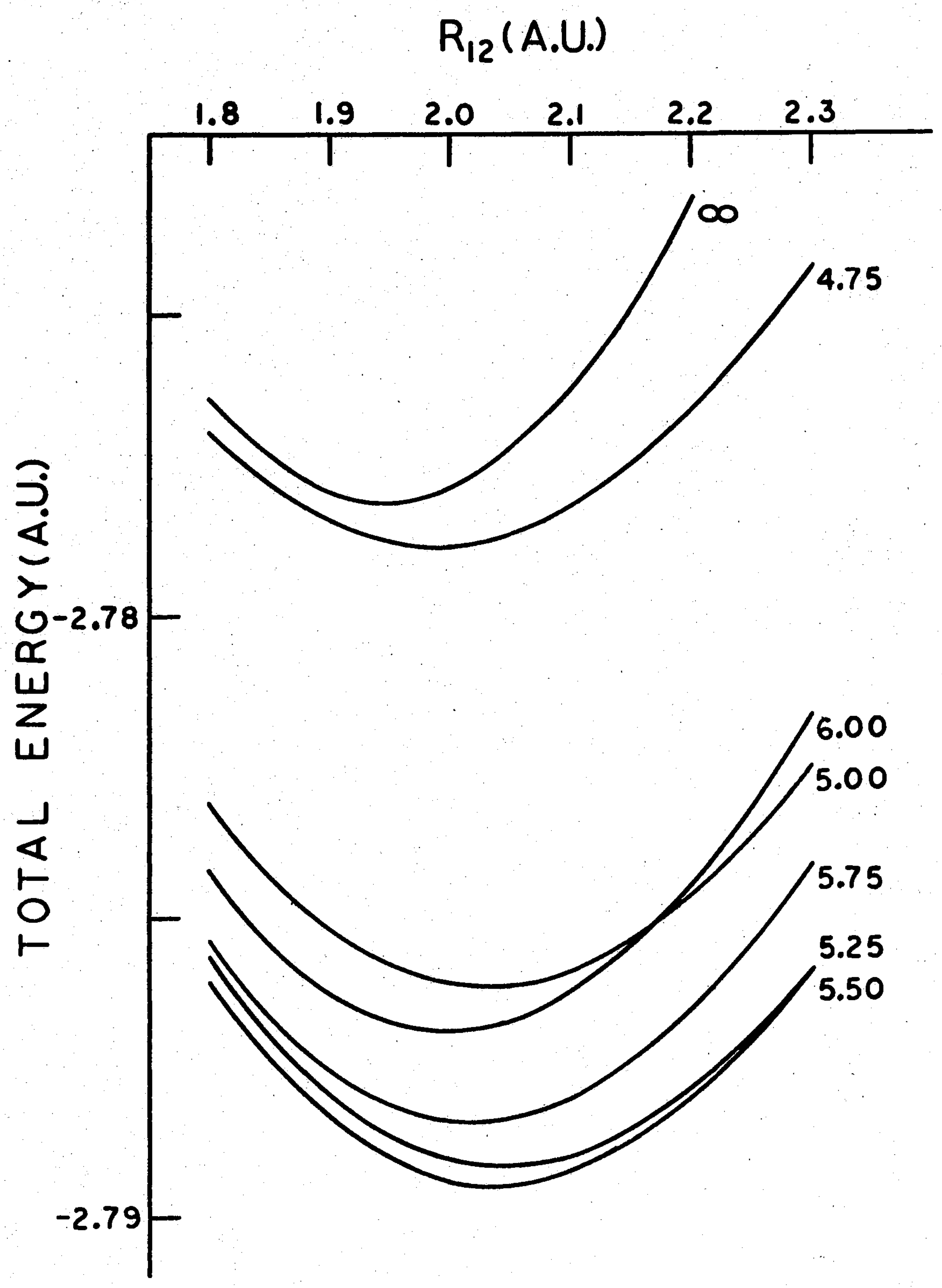

Figure 32. RDAO-1 Split Shell Total Energy vs. R_{12} for N-H··N

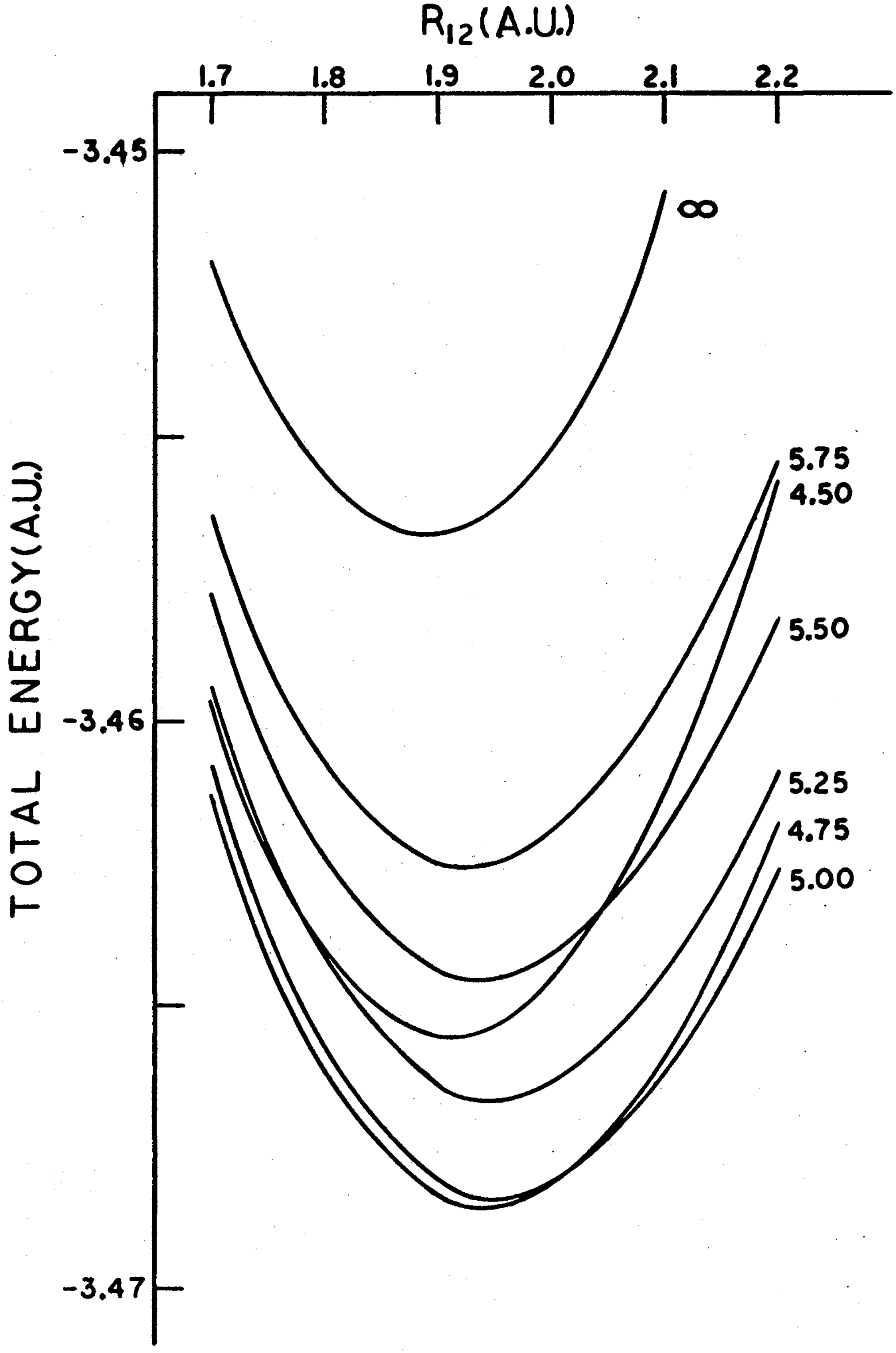

Figure 33. RDAO-1 Split Shell Total Energy vs. R_{12} for O-H··O

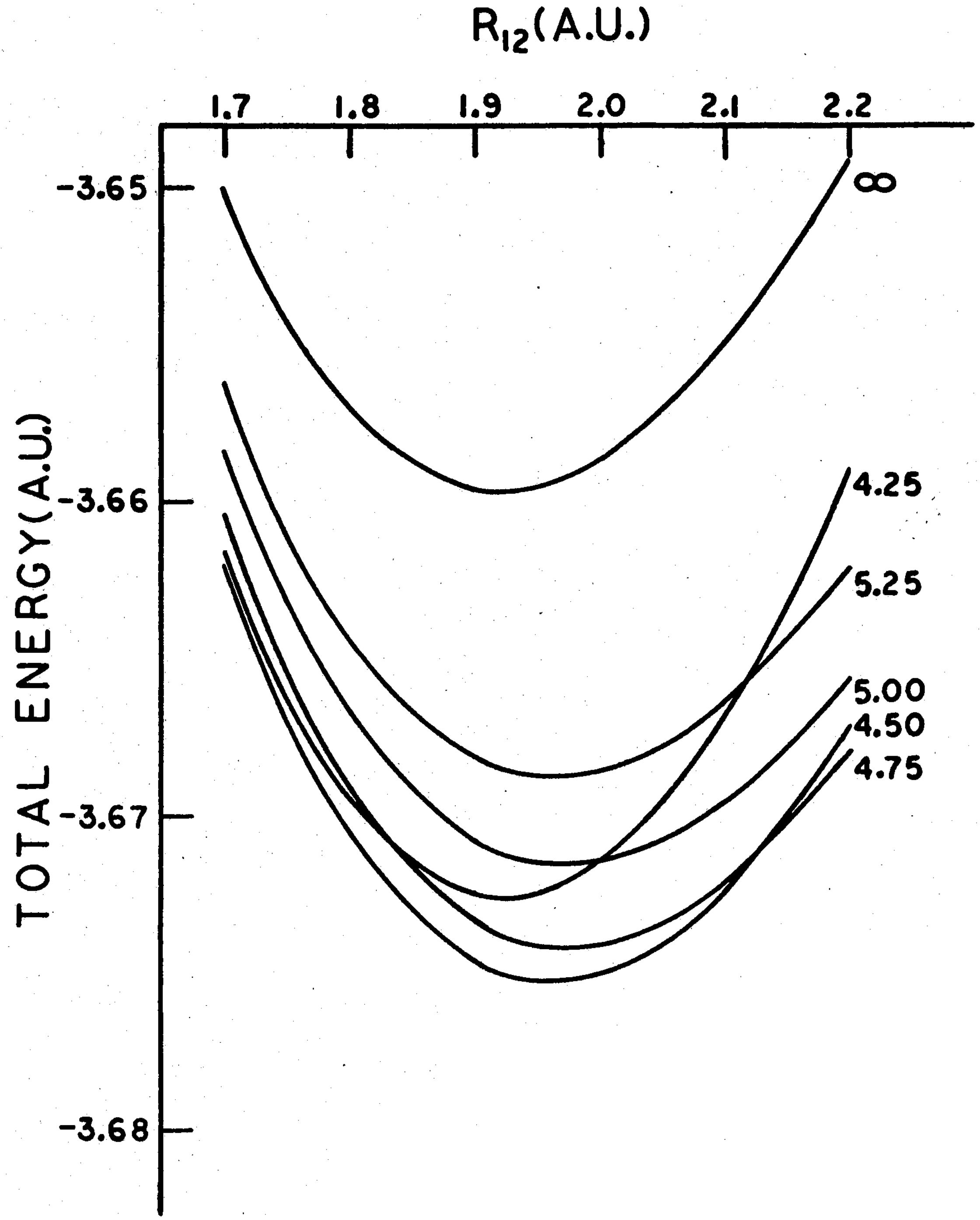

Figure 34. RDAO-1 Split Shell Total Energy vs. R_{12} for F-H··F

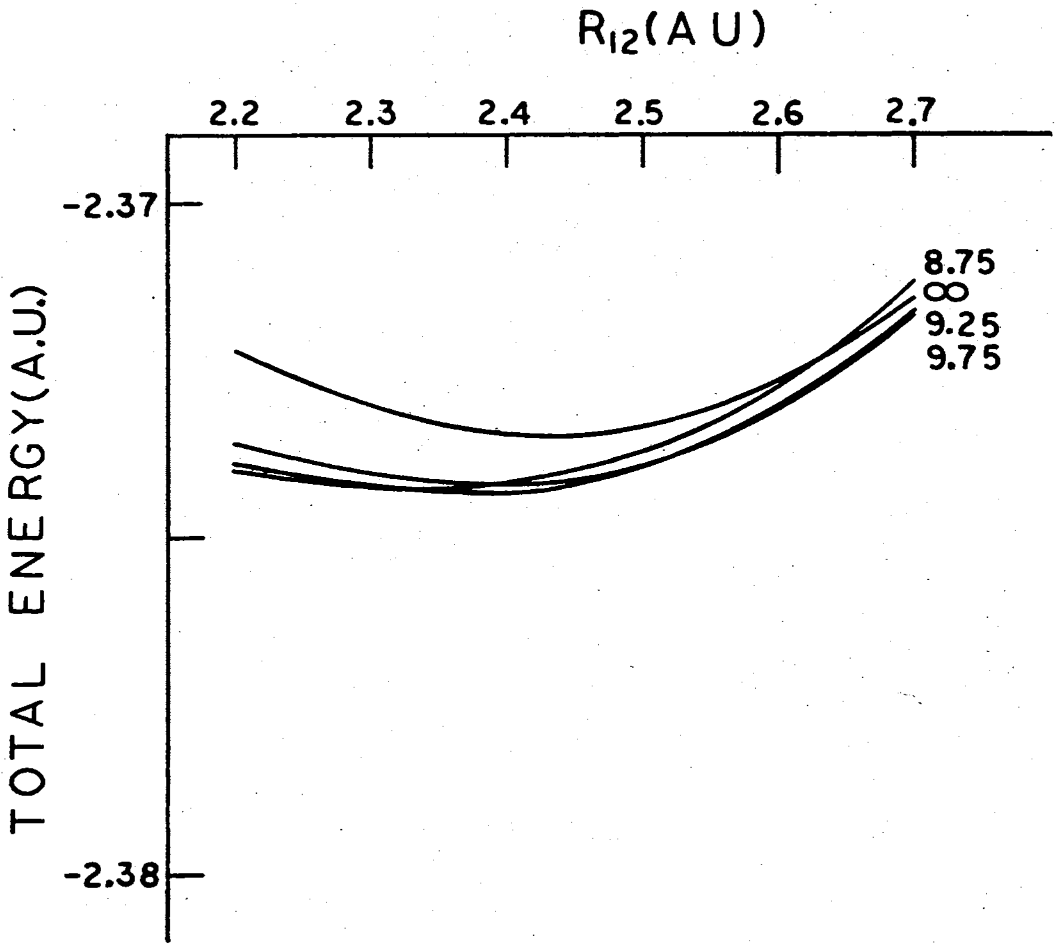

Figure 35. RDAO-1 Split Shell Total Energy vs. R_{12} for P-H··P

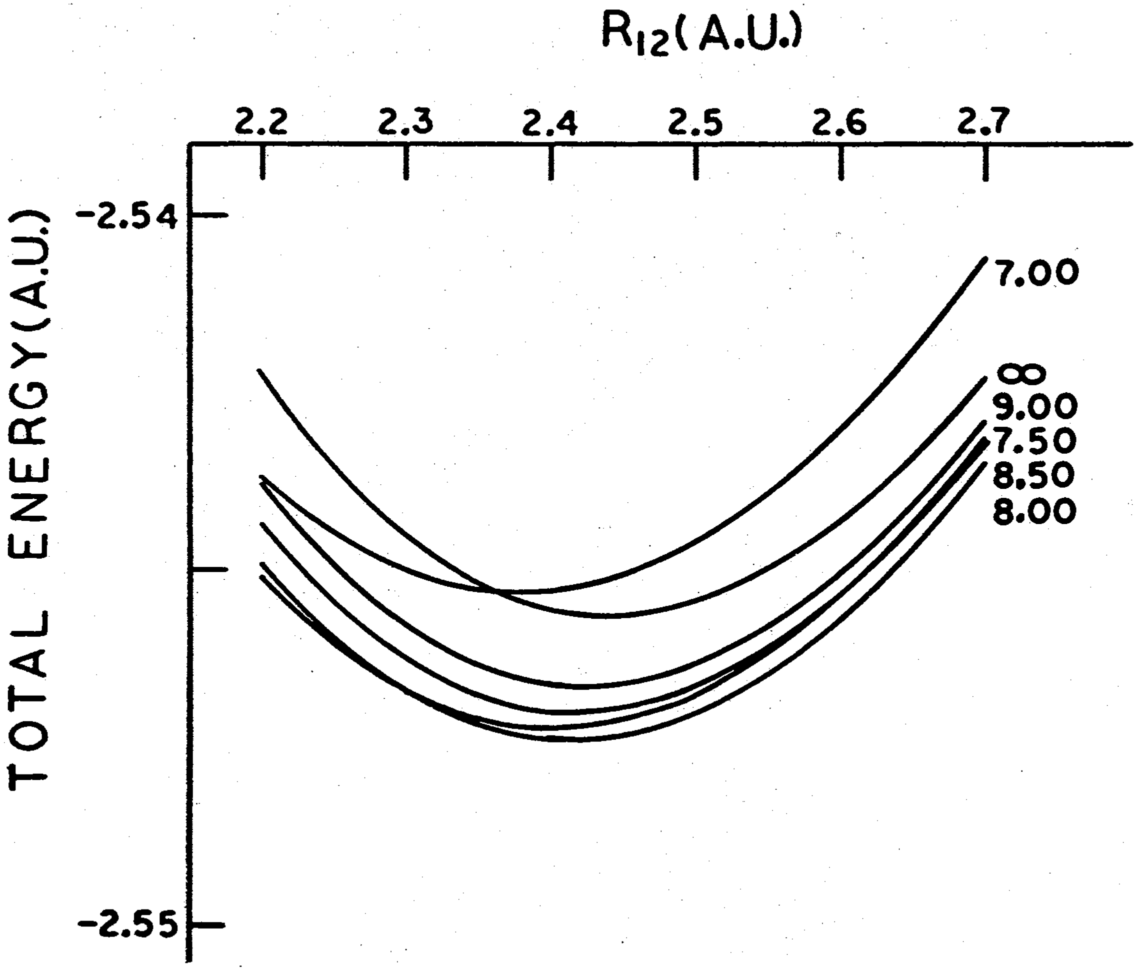

Figure 36. RDAO-1 Split Shell Total Energy vs. R_{12} for S-H··S

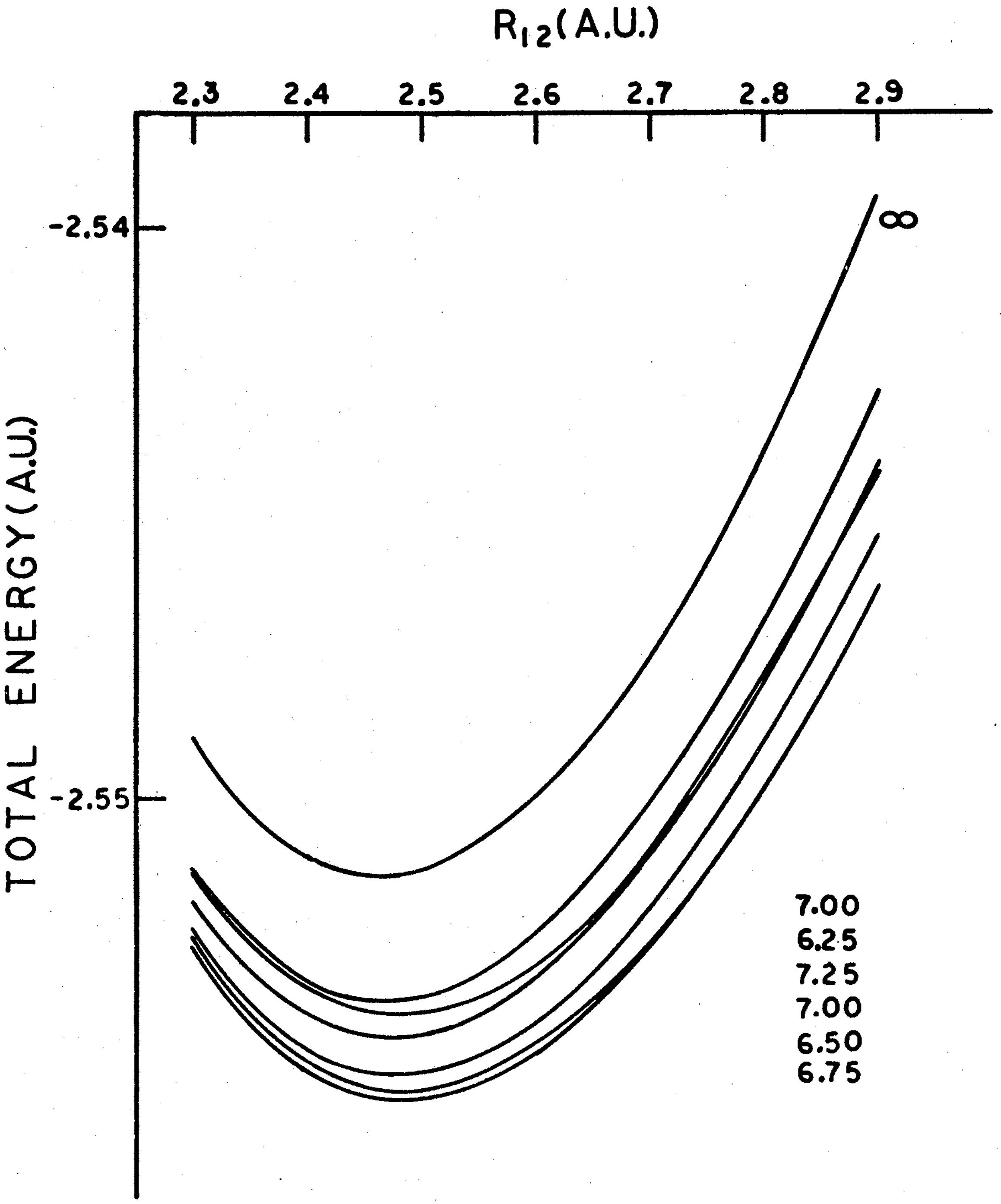

Figure 37. RDAO-1 Split Shell Total Energy vs. R_{12} for Cl-H··Cl

The maximum binding energies are sequenced in the order F $>$ O $>$ N $>$ Cl $>$ S $>$ P falling in the same order as the SCF and experimental dimer energies. The stabilization energies by the split method are about 1 kcal/mole higher than those given by the SCF method even to the extent of predicting binding for the P-H··P and S-H··S systems. The S-H··S stabilization energy agrees very well with the energy obtained experimentally by Lowder, et. al. (96) for the $(H_2S)_2$ dimer. The split shell results for S-H··S also contrast very well with the CNDP calculations of Sabin (61) on the linear $(H_2S)_2$ dimer which gave a stabilization energy of 21.6 kcal/mole for an S-S separation of 5.67 au and 5.86 au. The X-X separations are within 10% of the experimental dimer values except for the case of N-H··N where the split shell RDAO-1 is within 10% of the experimental average of 5.86 au. In comparison to the SCF results, the split shell results for R_{13} are all within 2% of the SCF results and all except the O-O separation are shorter.

The calculated X-H separations corresponding to the "monomers" are uniformally larger than the SCF results with the largest changes, those for the Cl-H and O-H systems, being only about 2% and 1.6% respectively. This is in accord with the results of Harris and Pohl (24) in comparing SCF and split shell calculations on the hydrogen halides. Again, all the experimental values are within 10% of the calculated values.

The split shell results for equilibrium X-H separations in the case of H-bonding are all slightly larger than the SCF results except for F-H··F where there is no change. Comparison with experimental data yields agreement within 5% for N, O and F. Somewhat surprising is the prediction of the contractions of the P-H and S-H lengths of 0.06 au and 0.02 au upon H-bond formation. Since there seems to be no experi-

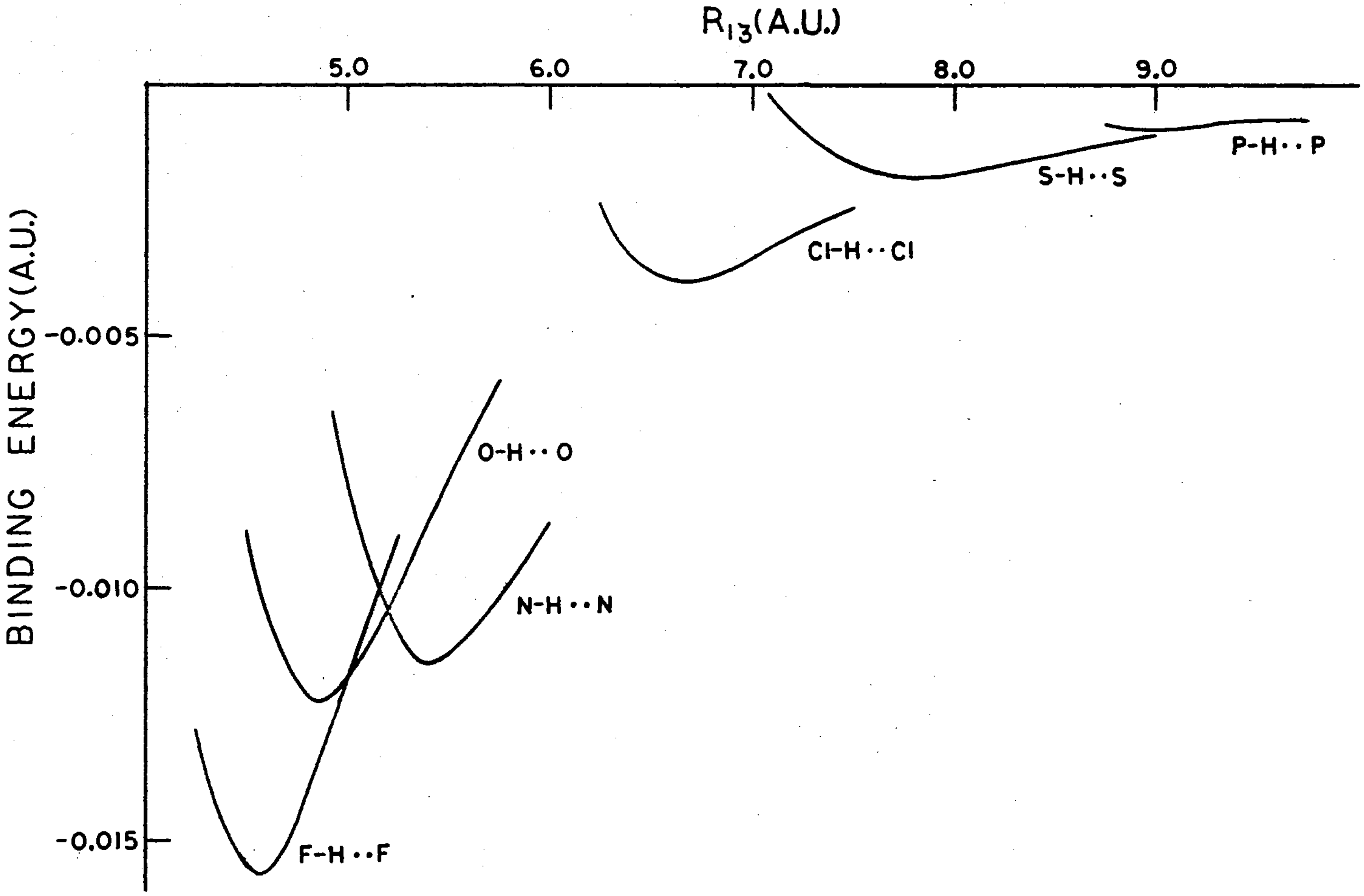

Figure 38. RDAO-1 Split Shell Binding Energies vs. R_{13} for X-H··X Systems

mental data with which to compare it is not known whether this contraction actually occurs.

The force constants for the X-H vibration are all smaller than the SCF values but still follow the experimental trend of $k_{S-H} < k_{Cl-H} < k_{N-H} < k_{O-H} < k_{F-H}$ with the force constants of the H-bonded systems showing the same trend. The ratios are a different sequence than are the SCF values following in the $N < 0 < F < Cl < S$ whereas the SCF ratios are in the order $N < F < 0 < Cl$. Further the split shell values are all smaller than the corresponding SCF values.

CHAPTER V

RDAO-2 CALCULATION ON FH

As a first attempt to formulate an analytical version of the RDAO method as applied to FH, the device of Weissmann and Cohan (44) of considering the valence shell electrons as static charge distributions was adopted. Tetrahedral hybridization of the flourine valence shell Slater AO's were assumed with two electrons assumed to be occupying each of the three AO's not involved in the bond. The 1s orbital was assumed for the H center. Figure 39 gives the configuration of the two nucleii AO's and coordinate system with R being the internuclear coordinate.

The hamiltonian operator for the two bonding electrons is then,

$$\textcircled{H} = \sum_{i=1}^{2} [-\tfrac{1}{2}\nabla_i^2 + V_f(i) + V_H(i)] + \frac{1}{r_{i2}} \tag{78}$$

where V_F is the electronic potential energy, and r_{12} is electron-electron separation. The potential operators V_F and V_H are

$$V_{Fi}^{(i)} = -\frac{7}{R_{Fi}} + 6[\int \frac{2te_2^{(2)}\,2te_2^{(2)}}{r_{i2}}\,d\tau_2] \tag{79}$$

and

$$V_H(i) = -\frac{1}{R_{Hi}} \tag{80}$$

where R_{Fi} is the distance of electron i from the F core, R_{Hi} is the distance of electron i from the H core, and r_{i2} id distance of electron i from an electron in one of the static charge distributions on the F core.

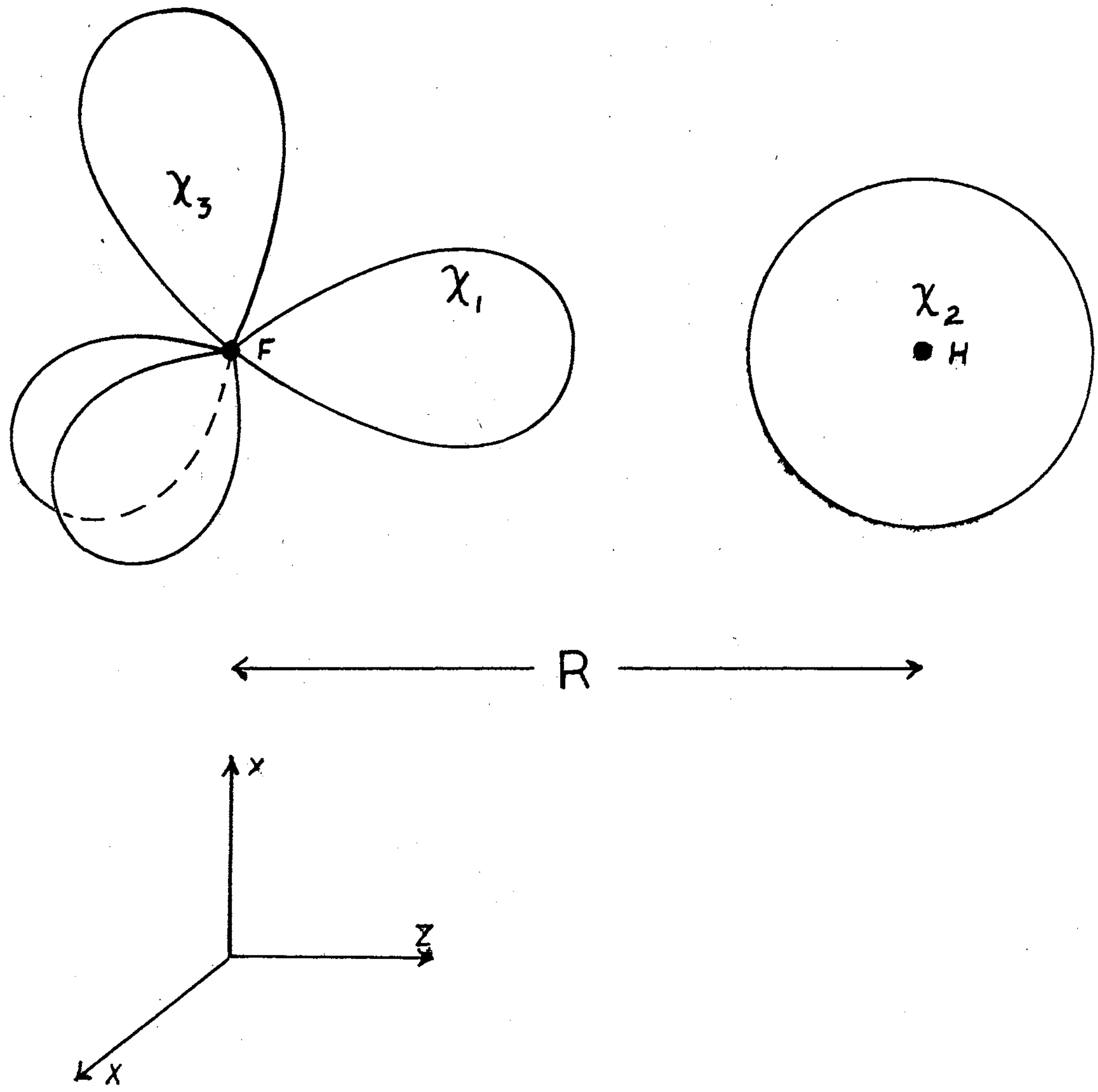

Figure 39. Schematic of F-H Problem

A closed shell wave function was assumed for the bonding electrons

$$\Psi = \psi\psi[\alpha\beta - \beta\alpha] \tag{81}$$

with the MO ψ being

$$\psi = c_1\chi_1 + c_2\chi_2 \tag{82}$$

where

$$\chi_1 = 2te_1 = \tfrac{1}{2}[2S_F + \sqrt{3}\ p_{zF}] \tag{83}$$

and

$$\chi_2 = 1S_H \ . \tag{84}$$

The total energy of the system at a particular value of R than is

$$E = \Sigma + \frac{7}{R} - 6\ <\chi_3|\frac{1}{R_{Hi}}|\chi_3> \tag{85}$$

where is the electronic energy and

$$\chi_3 = 2te_2 = \tfrac{1}{2}[2S_F + 2\sqrt{\tfrac{2}{3}}\ P_{zF} - \frac{P_{zF}}{\sqrt{3}}]. \tag{86}$$

A small FORTRAN IV program for this problem was written for this problem using the Roothaan SCF formulation described in Chapter II. The analytic values for the integrals involved were evaluated by the DIAT supplied by the Quantum Chemistry Program Exchange (97).

The results of this calculation are summarized in Table XII which lists the AO coefficients and energies and by Figure 40 which gives the total energy as a function of R. The model fails badly on two counts. The equilibrium R value of 1.47 au is much too small compared to the experimental value of 1.72 au. Also the binding energy when calculated as the difference between the energy of the separated atoms and the minimum total energy gives a value of 354 kcal/mol. as against an experimental value of 141 kcal/mole. These results are consistent with results of Weissmann and Cohann on the O-H..O system where they also obtained very short equilibrium bond lengths and high binding energies. Because of the failure of the method in this problem no attempt was made to compute the properties of $(FH)_2$.

TABLE XII

RDAO-2 TOTAL ENERGIES AND MO COEFFICIENTS FOR F-H

R(au)	E(au)	C_1	C_2
1.2	-1.9897	0.6089	0.5024
1.3	-2.0481	0.6119	0.5058
1.4	-2.0732	0.6155	0.5096
1.5	-2.0762	0.6198	0.5135
1.6	-2.0643	0.6251	0.5171
1.7	-2.0424	0.6311	0.5206
1.8	-2.0140	0.6379	0.5237

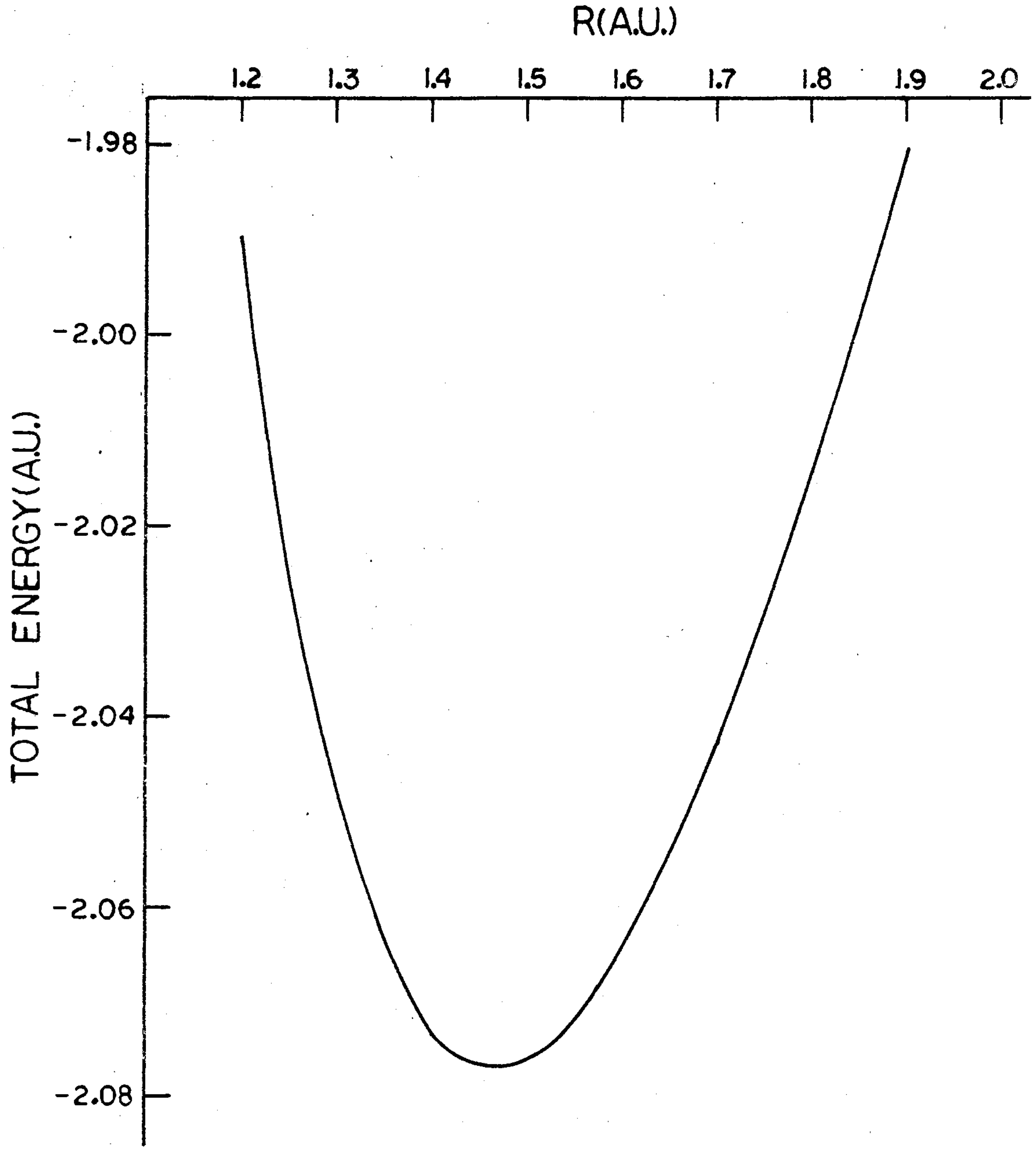

Figure 40. RDAO-2 SCF Total Energy vs. R for F-H System

CHAPTER VI

CONCLUSION

A technique for solving the Schroedinger equation for sigma electron systems was described and applied to hydrogen bonding between neutral molecules. The technique (known as the RDAO method) explicitly treats only those electrons assumed to be taking part in the bonding and neglects no integral in which these electrons are involved. This is in contrast to recent trends in methods for which all of the valence shell electrons are considered but neglect all exchange integrals or all but one center exchange integrals. A version utilizing semi-empiric evaluation of integrals (RDAO-1) and an analytic version (RDAO-2) were developed and applied, RDAO-1 to systems containing elements of the second and third rows of the periodic table and RDAO-2 to the molecule HF.

When applied to linear X-H··Y systems using an SCF closed shell wave function the RDAO-1 scheme yielded very good correlations with experiment for the binding energies, X-H bond lengths, X-H bond length shifts when bonding was assumed, X··Y bond lengths, X-H vibrational force constants, and qualitative weakening of this force constants under bonding conditions. The binding energies were generally within a few kcal/mol. of the experimental values and exhibited the correct experimental sequencing within homologous series. The results for the bond lengths and force constants also correlated well with experimental values and trends. Exception to these generally good results were systems in the series X-H··N for which disturbingly high binding energies at very short X··N distances were obtained. Also no prediction of binding was obtained for the P-H··P and S-H··S systems.

The application of the RDAO-1 method using a split shell wave function to linear X-H··X systems in general yielded binding energies which were slightly higher than those obtained in the closed shell calculations but again were sequenced in the correct experimental order. The prediction of bonding for the P-H··P and S-H··S systems was obtained in these calculations. X-H bond lengths were slightly larger than those obtained with the closed shell function, X··X bond lengths slightly smaller, and the X-H force constants smaller.

The RDAO-2 method assumed that the valence shell electrons on the F core considered to be not involved in the bonding were static charge distributions centered on the F core. A closed shell SCF calculation on the FH bond using analytic values for the integrals involved yielded a binding energy about three times the experimental value at a very short bonding distance.

The semiempirical results were obtained without any arbitrary adjustment of the parameters used in the evaluation of integrals. The good agreement of calculated properties with experimental values indicates that the integral approximations used form a good description of the molecular system in regions around the experimental separations. In regions of close approach these approximations break down. Better agreement with experiment could probably be achieved by a slightly different set of parameters. In particular, the parameters used to describe the lone pair of electrons on the nitrogen core seem to be incorrect.

The use of a split shell wave function as formulated here would seem to be limited to systems with small numbers of electrons. The increase in the number of AO's necessary to provide a different MO for each electron leads to a tremendous increase in the number of basis VB functions with a consequent increase in programing labor and computer time. The problem would grow to unwieldy proportions for practical considerations for systems with more than four electrons.

One other facet of the RDAO-1 method which deserves comment is that unlike most of the methods described in Chapter I it is independent of quantities such as the Wolfsberg-Helmholz parameter and parameters which depend upon the identity of atom pairs. A single core is described throughout the problem by a single set of parameters. The RDAO-1 method thus has much less arbitrariness associated with it than do other methods.

In conclusion, the success of the RDAO-1 method in this study warrants its application to other systems in which a sigma electron system is involved. The RDAO-2 method on the other hand requires considerably more development before it can be considered to have any degree of reliability.

BIBLIOGRAPHY

1. Hückel, E.; Z. Physik 70, 204 (1931).
2. Hückel, E.; Z. Physik 76, 628 (1932).
3. Hückel, E.; Trans. Faraday Soc. 30, 40 (1934).
4. Pariser, R. and Parr, R. G.; J. Chem, Phys. 21, 466 (1953).
5. Pariser, R. and Parr, R. G.; J. Chem. Phys. 21, 767 (1953).
6. Pople, J. A.; Trans. Faraday Soc. 49, 1375 (1953).
7. Hoffmann, R.; J. Chem. Phys. 39, 1397 (1963).
8. Rein, R., Fukuda, H., Win, H., Clarke, G. A., and Harris, F. E.; J. Chem. Phys. 45, 4743 (1966).
9. Pople, J. A., Santry, D. P., and Segal, G. A.; J. Chem. Phys. 43, S129 (1965).
10. Pople, J. A. and Segal, G. A.; J. Chem. Phys. 43, S136 (1965).
11. Pople, J. A. and Segal, G. A.; J. Chem. Phys. 44, 3289 (1966).
12. Santry, D. P. and Segal, G. A.; J. Chem. Phys. 47, 158 (1967).
13. Pople, J. A., Beveridge, D. L., and Dobosh, P. A.; J. Chem. Phys. 47, 2026 (1967).
14. Klopman, G.; J. Am. Chem. Soc. 86, 330 (1964).
15. Klopman, G.; J. Am. Soc. 86, 4550 (1964).
16. Klopman, G.; J. Am. Chem. Soc. 87, 3300 (1965).
17. Dewar, M. J. S. and Klopman, G.; J. Am. Chem. Soc. 89, 3089 (1967).
18. Baird, N. C. and Dewar, M. J. S.; J. Am. Chem. Soc. 89, 3966(1967).
19. Baird, N. C. and Dewar, M. J. S.; Theoret, Chim. Acta. 9, 1 (1967).
20. Baird, N. C. and Dewar, M. J. S.; J. Chem. Phys. 50, 1275 (1969).
21. Baird, N. C., Dewar, M. J. S., and Sustmann, R.; J. Chem. Phys. 50, 1262 (1969).

22. Dixon, R. N.; Mol. Phys. 12, 83 (1967).

23. Pohl, H. A., Rein, R., Appel, K.; J. Chem. Phys. 41, 3385 (1964).

24. Harris, F. E. and Pohl, H. A.; J. Chem. Phys. 42, 3648 (1965).

25. Pohl, H. A. and Raff, L. M.; Int. J. Quant. Chem. 1, 577 (1967).

26. Mickish, D. J. and Pohl, H. A.; "Simplified SCF Calculations for Sigma-Bonded Systems: Extension to Hydrogen Bonded Systems." Sigma Molecular Orbital Theory. Ed. Oktay Sinanoglu and Kenneth B. Widberg. New Haven: Yale University Press, 1970, 105-114.

27. Pimentel, G. and McClellan, A. L.; The Hydrogen Bond, W. H. Freeman and Company, San Francisco, 1960.

28. Löwdin, P. O.; Rev. Mod. Phys. 35, 724 (1963).

29. Lippincott, E. R. and Schroeder, R.; J. Chem. Phys. 23, 1099 (1955).

30. Schroeder, R. and Lippincott, E. R.; J. Phys. Chem. 61, 921 (1957).

31. Reid, C.; J. Chem. Phys. 30, 182 (1959).

32. Clementi, E.; J. Chem. Phys. 46, 3851 (1967).

33. Clementi, E.; J. Chem. Phys. 47, 2323 (1967).

34. Clementi, E. and Gayles, J. N.; J. Chem. Phys. 47, 3837 (1967).

35. van Duijneveldt, F. B. and Murrell, J. N.; J. Chem. Phys. 46, 1759 (1967).

36. van Duijneveldt-van de Rijdt, J. G. C. M. and van Duijneveldt, F. B.; Chem. Phys. Letters 2, 565 (1968).

37. Shaw, G.; International J. Quant. Chem. III, 219 (1969).

38. Coulson, C. A. and Danielsson, U.; Arkiv Für Fysik 8, 239 (1954); 254 (1954).

39. Tsubormura, H.; Bull. Chem. Soc. Jap. 27, 445 (1954).

40. McKinney, P. C. and Barrow, G. M.; J. Chem. Phys. 31, 294 (1959).

41. Hasegawa, M., Daiyasu, K., and Yomosa, S.; J. Jap. Phys. Soc. 27, 999 (1969).

42. Hasegawa, M., Daiyasu, K., and Yomosa, S.; J. Jap. Phys. Soc. 28, 1304 (1970).

43. Yomosa, S. and Hasegawa, M., J. Jap. Phys. Soc. 29, 1329 (1970).

44. Weissmann, M. and Cohan, N. V.; J. Chem. Phys. 43, 119 (1965); 124 (1965).

45. Paoloni, L.; J. Chem. Phys. 30, 1045 (1959).

46. Fischer-Hjalnars, I. and Grahn, R., Acta Chem. Scand. 12, 584 (1958).

47. Grahn, R.; Arkiv Für Fysik 15, 257 (1959).

48. Clementi, E. and McLean, A. D., J. Chem. Phys. 36, 745 (1962).

49. Morokuma, K. and Pederson, L.; J. Chem. Phys. 48, 3275 (1968).

50. Kollman, P. A. and Allen, L. C.; J. Chem. Phys. 51, 3286 (1969).

51. Kollman. P. A. and Allen, L. C.; J. Am. Chem. Soc. 92, 6101 (1970).

52. Kollman, P. A. and Allen, L. C., J. Chem. Phys. 52, 5085 (1970).

53. Dierksen, G. H. F. and Kraemer, W.; Chem. Phys. Lett. 5, 57 (1970).

54. Kraemer, W. and Dierksen, G. H. F.; Chem. Phys. Lett. 5, 463 (1970).

55. Dierksen, G. H. F. and Kraemer, W.; Chem. Phys. Lett. 6, 419 (1970).

56. Dierksen, G. H. F.; Theoret. Chim. Acta (Berl.) 21, 335 (1971).

57. Morokuma, K. and Winick, J. R.; J. Chem. Phys. 52, 1301 (1970).

58. Morokuma, K.; J. Chem. Phys. 55, 1236 (1971).

59. Hoyland, J. R. and Kier, L. B.; Theoret. Chim. Acta (Berl.) 15, 1 (1969).

60. Kollman, P. A. and Allen, L. C.; J. Am. Chem. Soc. 92, 754 (1970).

61. Sabin, J.; J. Am. Chem. Soc. 93, 3614 (1971).

62. Rein, R., Clarke, G. A., and Harris, F. E.; J. Mol. Structure 2, 103 (1968).

63. Murthy, A. S. N. and Rao, C. N. R.; Chem. Phys. Lett. 2, 123 (1968).

64. Rein, R., and Harris, F. E.; J. Chem. Phys. 41, 3393 (1964).

65. Rein, R., and Harris, F. E.; J. Chem. Phys. 42, 2177 (1965).

66. Rein R. and Harris, F. E.; J. Chem. Phys. 43, 4415 (1965).

67. Lunell, S. and Sperber, G.; J. Chem. Phys. 46, 2119 (1967).

68. Coulson, C. A. and Fischer, I.; Phil. Mag. 40, 386 (1949).

69. Harris, F. E., Micha, D. A., and Pohl, H. A.; Arkiv Für Fysik 30, 259 (1965).

70. Slater, J. C.; Phys. Rev. 36, 57 (1930).

71. Zener, C.; Phys. Rev. 36, 51 (1930).

72. Coulson, C. A.; Valence London, Oxford University Press, 1961.

73. Roothaan, C. C. J.; Rev. Mod. Phys. 23, 69 (1951).

74. Löwdin, P. O.; Rev. Mod. Phys. 36, 966 (1964).

75. See, e.g., Rose, M. E.; Elementary Theory of Angular Momentum, John Wiley and Sons, New York, 1961.

76. Löwdin, P. O.; "Spin Degeneracy Problem", Technical Note of the Quantum Chemistry Group for Research in Atomic, Molecular, andSolid State Theory. University of Uppsala, Uppsala, Sweden. Special issue prepared for the 1961/62 Winter Institute in Quantum Chemistry and Solid State Physics at the University of Uppsala.

77. Mullikan, R. S., Reike, C. A., Orloff, D., and Orloff, H.; J. Chem. Phys. 17, 1248 (1949).

78. Ballhausen, C. J. and Gray, H. B.; Molecular Orbital Theory, W. A. Benjamin, Inc., New York, 1965, p. 269.

79. Goeppert-Meyer, M. and Sklar, A. L.; J. Chem. Phys. 41, 3385 (1964).

80. Mullikan, R. S., J. Chem. Phys. 46, 497 (1949).

81. Pariser, R.; J. Chem. Phys. 21, 568 (1953).

82. Hinze, J. and Jaffé, H. H.; J. Am. Chem. Soc. 84, 540 (1962).

83. Pohl, H. A., Private communication.

84. Roothaan, C. C. J.; J. Chem. Phys. 19, 1445 (1951).

85. Herman, F. and Skillman, S.; Atomic Structure Calculations, Prentice-Hall, Englewood Cliffs, N. J., 1963.

86. Mickish, D. J.; Private communication.

87. Michels, H. H., van Dine, C. P., and Elliot, P. E.; Quantum Chemistry Program Exchange No. 97, "CEIG".

88. Prosser, F.; Quantum Chemistry Program Exchange No. 62.1, "GIVENS".

89. Löwder, J.; Quant. Spectrosc. Radiat. Transfer 10, 1085 (1970).

90. Murthy, A. S. N., and Rao, C. N. R.; Appl. Spectroscopy Rev. 2, 69 (1968).

91. Smith, D. F. J.; J. Mol. Spectrosc. 3, 479 (1959).

92. *Tables of Interatomic Distances and Configurations in Molecules and Ions*. Special Publication No. 11, Chemical Society, Burlington House, London 1958.

Interatomic Distances Supplement. Special Publication No. 18, Chemical Society, Burlington House, London, 1965.

93. Srinivasan, R., and Chacko, K. K.; Conform. Biopolym., Pap. Int. Symp., Madras 1967, 2, 607-15.

94. Harada, J., and Kitamura, N.; J. Phys. Soc. Jap. 19, 328 (1964).

95. Herzberg, G.; *Spectra of Diatomic Molecules*, D. van Nostrand Company, Inc., Princeton, 1957.

96. Löwder, J. E., Kennedy, L. A., Sulzmann, K. G. P., Penner, S. S.; J. Quant. Spectrosc. Radiat. Transfer 10, 17 (1970).

97. Switendick, A. C. and Corbató, F. J.; Quantum Chemistry Program Exchange No. 29 "DIAT".

APPENDIX A

CONSTRUCTION OF THE SPIN FUNCTIONS

The spin functions for the system of four electrons can be constructed using the projection operator technique of Löwdin (74). An operator is defined which, when applied to a general spin function, projects out the desired component associated with a particular total spin quantum number S and its z-component M_s. If $\textcircled{H}$ is the general function where

$$\textcircled{H} = \sum_{S_i, M_{s_i}} \textcircled{H}_{S_i\, M_{s_i}}$$

and $\textcircled{H}_{S_i, M_i}$ is the spin eigenfunction associated with the spin quantum numbers S_i and M_{S_i}, then an operator O_{S,M_S} is constructed such that

$$O_{sMs}\textcircled{H} = \textcircled{H}_{S,\, M_s} .$$

The general form of the operator O_{S,M_S} in the case $S = M_s$ is derived in reference 75 to be

$$O_{SS} = (2S+1)! \sum_{\nu=o}^{S_{Max}-s} (-1)^{\nu} \frac{M^{\nu} M_+^{\nu}}{\nu!(2S+\nu+1)!}$$

where S_{Max} is the maximum value of S for the system and M_- and M_+ are the usual "step-up" and "step-down" (75) operators with the properties

$$M_{\pm} \textcircled{H}_{sMs} = [(S \mp M_s)(S \pm M_s + 1)]^{\frac{1}{2}} \textcircled{H}_{s,\, M_{s\pm1}}. \qquad \text{(A-1)}$$

For the case of interest here, $S = M_s = 0$ and the operator O_{oo} can be written explicitly as

$$O_{oo} = 1 - \tfrac{1}{2} M_- M_+ + 1/12\, M_-^2 M_+^2 \quad . \qquad \text{(A-2)}$$

The basis set consists of all linearly independent products of the four single particle spin functions α and β for which $M_s = 0$. There are six of these products which, listed in lexocographic order, are

$$\begin{aligned} \nu_1 &= \alpha\alpha\beta\beta \\ \nu_2 &= \alpha\beta\alpha\beta \\ \nu_3 &= \alpha\beta\beta\alpha \\ \nu_4 &= \beta\alpha\alpha\beta \\ \nu_5 &= \beta\alpha\beta\alpha \\ \nu_6 &= \beta\beta\alpha\alpha \end{aligned} \tag{A-3}$$

There will be six projected functions

$$\textcircled{H}_i = O_{oo}\,\nu_2$$

for which $S = M = 0$, but only two of these will be linearly independent as seen from the following argument (76). Considering the spin functions $\alpha\alpha\alpha\beta$, $\alpha\alpha\beta\alpha$, $\alpha\beta\alpha\alpha$, and $\beta\alpha\alpha\alpha$, it is clear that they have no $S = 0$ component since $M_s = 1$ for each function. Therefore, neither do the functions $M_-\alpha\alpha\alpha\beta$, $M_-\alpha\alpha\beta\alpha$, $M_-\alpha\beta\alpha\alpha$, and $M_-\beta\alpha\alpha\alpha$ since the "step down" operator changes only the M_s value associated with the spin function. Applying the operator O_{oo} to these four functions and using the relations

$$M_\pm = M_\pm(1) + M_\pm(2) + M_\pm(3) + M_\pm(4) \tag{A-4}$$

and

$$\begin{aligned} M_+(i)\alpha(i) &= 0 \qquad & M_-(i)\alpha(i) &= \beta(i) \\ M_+(i)\beta(i) &= \alpha(i) \qquad & M_-(i)\beta(i) &= 0 \end{aligned} \tag{A-5}$$

four relations among the functions (A-3) are obtained,

$$\begin{aligned} \textcircled{H}_1 + \textcircled{H}_2 + \textcircled{H}_4 &= 0 \\ \textcircled{H}_1 + \textcircled{H}_3 + \textcircled{H}_5 &= 0 \end{aligned}$$

$$\textcircled{H}_2 + \textcircled{H}_3 + \textcircled{H}_6 = 0$$

$$\textcircled{H}_4 + \textcircled{H}_5 + \textcircled{H}_6 = 0$$

As an example,

$$\begin{aligned} M_-\alpha\alpha\alpha\beta &= M_-(1)\alpha\alpha\alpha\beta + M_-(2)\alpha\alpha\alpha\beta + M_-(3)\alpha\alpha\alpha\beta + M_-(4)(\alpha\alpha\alpha\beta \\ &= \beta\alpha\alpha\beta + \alpha\beta\alpha\beta + \alpha\alpha\beta\beta + 0. \end{aligned}$$

Therefore,

$$\begin{aligned} O_{oo}M_-\alpha\alpha\alpha\beta &= O_{oo}\beta\alpha\alpha\beta + O_{oo}\alpha\beta\alpha\beta + O_{oo}\alpha\alpha\beta\beta \\ &= \textcircled{H}_4 + \textcircled{H}_2 + \textcircled{H}_1 = 0. \end{aligned}$$

The other three relations following a similar manner. These four relations may also be solved as

$$\textcircled{H}_1 = \textcircled{H}_6,\ \textcircled{H}_2 = \textcircled{H}_5,\ \textcircled{H}_3 = \textcircled{H}_4,\ \text{and}$$

$$\textcircled{H}_1 + \textcircled{H}_2 + \textcircled{H}_3 + \textcircled{H}_4 + \textcircled{H}_5 + \textcircled{H}_6 = 0.$$

Only two of these functions need therefore to explicitly be constructed and the ones chosen were $\textcircled{H}_1$ and $\textcircled{H}_2$. The construction $\textcircled{H}_1$ is shown below using equations (A-2), (A-4) and (A-5).

Applying the "step-up" operator to $\alpha\alpha\beta\beta$,

$$M_+\ \alpha\alpha\beta\beta = \alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha$$

and

$$M_+^2\alpha\alpha\beta\beta = 2\alpha\alpha\alpha\alpha. \tag{A-6}$$

Similarly,

$$M_-M_+\alpha\alpha\beta\beta = \beta\alpha\alpha\beta + \alpha\beta\alpha\beta + 2\alpha\alpha\beta\beta + \beta\alpha\beta\alpha + \alpha\beta\beta\alpha$$

$$M_-M_+^2\alpha\alpha\beta\beta = 2(\beta\alpha\alpha\alpha + \alpha\beta\alpha\alpha + \alpha\alpha\beta\alpha + \alpha\alpha\alpha\beta) \tag{A-7}$$

and

$$M_-^2M_+^2\alpha\alpha\beta\beta = 4(\alpha\alpha\beta\beta + \beta\beta\alpha\alpha + \alpha\beta\alpha\beta + \beta\alpha\beta\alpha + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta). \tag{A-8}$$

For $\textcircled{H}_1$, then,

$$\textcircled{H}_1 = O_{oo}\nu = O_{oo}\alpha\alpha\beta\beta = [1 - \tfrac{1}{2} M_-M_+ + 1/12\, M_-^2M_+^2]\,\alpha\alpha\beta\beta .$$

Solving,

$$\textcircled{H}_1 = 1/3[\alpha\alpha\beta\beta + \beta\beta\alpha\alpha] - 1/6[\alpha\beta\alpha\beta + \beta\alpha\beta\alpha + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta].$$

The second spin function can be constructed similarly to be

$$\textcircled{H}_2 = O_{oo}\alpha\beta\alpha\beta = 1/3[\alpha\beta\alpha\beta + \beta\alpha\beta\alpha] - 1/6\,[\alpha\alpha\beta\beta + \beta\beta\alpha\alpha + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta].$$

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VITA

Jerry Merle Cantril

Candidate for the Degree of

Doctor of Philosophy

Thesis: EXTENSION OF A SIMPLIFIED CALCULATIONAL METHOD FOR SIGMA BONDED SYSTEMS TO HYDROGEN BONDING AMONG ELEMENTS OF THE SECOND AND THIRD ROWS

Major Field: Physics

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Personal Data: Born in Hayden, Colorado, May 26, 1939, the son of William Merle and Annie Marguerite Cantril.

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