

A REJECTED HAMILTONIAN APPROACH  
TO POLYATOMIC SYSTEMS

By

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to  
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A method of treating polyatomic systems, finite or extended, is presented which fully exploits their "atom-in-molecule" nature. Within an independent-particle model a partitioning technique is applied to the projection of the full polyatomic space into many atomic subspaces. The subspaces are then each coupled to one another approximately through second-order in overlap in a piecewise self-consistent fashion. The inherent localized picture allows for an approximate form of the interatomic interactions without resorting to neglect of any differential overlap or use of any empirical parameters. Molecular orbitals and energies may be obtained from an approximate electron propagator which is based on a model Hamiltonian built up

from atomic one-electron Hamiltonians in diagonal form. Symmetric orthonormalization of these orbitals gives a density matrix which can be used as a guide for charge redistribution within the system. A generalization of the Hartree-Fock approximation based on a statistical ensemble is employed which permits the use of fractional occupation numbers in the atomic configurations. Application of the method here includes the nitric oxide molecule and its chemisorption on a nickel(100) surface.



CHAPTER I  
INTRODUCTION

In the quantum mechanical treatment of polyatomic systems, whether they be finite or extended, one feature consistently emerges, and that is they appear to be built up from "atoms". The reasonable success of the cellular (Slater, 1934), valence-bond (VE) (Cerratt, 1974), atom-in-molecule (AIM) (Moffitt, 1951), and similar building-block (Adams, 1971; Gilbert, 1972) approaches is indebted to this feature. However, as one progresses from atoms to molecules serious complications are encountered in the numerical and analytic techniques which have been so successfully applied to atoms. These complications are largely due to the loss of spherical symmetry and one-center expansions. For numerical techniques, the threat of multidimensional integrations and quadratures has led to cellular approximations to the potential (Slater, 1934) and local approximations to the exchange interactions (Slater, 1971). On the other hand, analytic methods are faced with the tremendous number of complicated multicenter two-electron

integrals, and one is usually forced to sacrifice both quality and quantity in the selection of basis sets (Dunning and Hay, 1977). The exclusion of core electrons by means of effective potentials (Kahn et al., 1976) has become a popular means of reducing the number of integrals. A whole gamut of semiempirical methods have also been devised and constantly revised to help overcome these difficulties.

One wonders, though, whether or not the ability to even describe the "atoms" within a system is lost in all these sacrifices. This brings us to the theme of the present work. We wish to maintain as much as possible a complete and accurate description of the "atoms" in a system at the controlled expense of an approximate, but sufficiently rigorous, nonempirical treatment of the interatomic interactions. Some corollaries to this theme will be to keep, intact, the molecular Hamiltonian while partitioning the discrete eigenspace (the finite space spanned by the discrete eigenfunctions) of an effective one-electron operator; to employ analytic techniques enabling proper treatment of the exchange interactions; to use suitable basis sets, such as Slater-type orbitals (STO's) of at least "double-zeta" (DZ) quality with polarization functions (DZP) when needed; to correctly compute and retain all one-center integrals and all two-center one-electron integrals; to reduce all multicenter two-electron integrals to two-center

one-electron integrals by exploiting the localized picture, but without resorting to empiricism or neglect of any differential overlap; and to establish atomic valency as a better-defined and workable concept.

In the next chapter the effective one-electron Hamiltonian operator and the partitioning of its eigenspace will be developed. Chapter III will deal more explicitly with the pseudopotential which is derived from the partitioning in chapter II. The approximate forms of the interatomic Coulombic and exchange interactions are given in chapters IV and V. Chapter VI is devoted to the piecewise construction of a model molecular one-electron Hamiltonian which when used in the moment expansion of the electron propagator gives rise to a model Fock matrix as its first moment. Solution of the corresponding eigenvalue problem is discussed together with an appropriate population analysis for redistributing electronic charge. In chapter VI a more general form of the Hartree-Fock approximation is described which allows for the definition of a self-consistent potential from a density corresponding to a statistical ensemble with specified occupation numbers. The problem of spin-orbital occupation assignments is the topic of chapter VIII. In chapter IX the method is applied to nitric oxide and its chemisorption on a nickel(100) surface. Separate treatments for the nitric oxide molecule, the nickel metal,

and the nickel(100) surface are included to emphasize the applicability of the method to various systems. The final chapter is a general discussion of some pros and cons of the method and some ideas for future work to alleviate any shortcomings the method might have.

## CHAPTER II

### THE EFFECTIVE ONE-ELECTRON OPERATOR AND THE PARTITIONING OF ITS EIGENSPACE

In order to illustrate the partitioning of a polyatomic system into many atomic subspaces it is sufficient, at least for the moment, to consider a diatomic molecule, A-B. In much of what is about to follow, specific attention will be focused on the case of a diatomic molecule. This is done strictly for clarity, and generalization to polyatomic systems shall be made at various times. The method is by no means restricted to diatomic molecules, even though its generalization might not appear obvious at times. In connection with this, we will mostly be concentrating on a single atom (A) at any one time, while the remaining atoms (B) will be considered as its environment. We shall usually denote this by the use of superscripts A or B, respectively; but when no specific reference is made, atom A is to be assumed. For cases other than diatomics, primes will also be used. See Figure 1 for other notation conventions to be adhered to throughout this and remaining chapters.

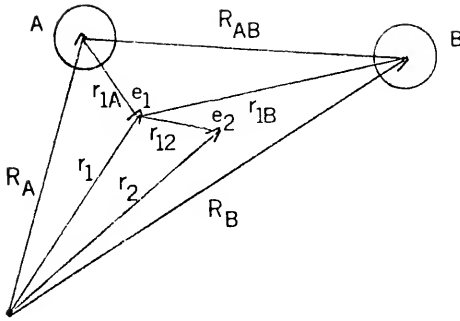


Figure 1. Electronic and nuclear coordinates for the diatomic molecule A-B.

The average value of the nonrelativistic many-electron Hamiltonian, with respect to a proper choice of density operator (see chapters VI and VII), for the diatomic molecule can be written in second quantization as

$$\begin{aligned}
 \langle H \rangle = & \sum_i^{(A)} h_i \langle a_i a_i \rangle + 1/2 \sum_{ij}^{(A)} (J_{ij} - K_{ij}) \langle a_i a_i a_j a_j \rangle \\
 & + \sum_i^{(B)} h_i \langle b_i b_i \rangle + 1/2 \sum_{ij}^{(B)} (J_{ij} - K_{ij}) \langle b_i b_i b_j b_j \rangle \\
 & + 1/2 \sum_i^{(A)} \sum_j^{(B)} (J_{ij} - K_{ji}) \langle a_i b_j b_j a_i \rangle \\
 & + 1/2 \sum_j^{(B)} \sum_i^{(A)} (J_{ji} - K_{ij}) \langle b_j a_i a_i b_j \rangle
 \end{aligned} \tag{II-1}$$

where the a's and b's are field operators corresponding to spin-orbitals assigned to atoms A and B, respectively, and the summations have been restricted accordingly. Let us assume that the spin-orbitals assigned to atom A are

expanded in a basis centered on A and the spin-orbitals assigned to atom B are likewise centered on B. Such a total energy functional leads to the effective one-electron operator

$$F_1 = -1/2 \nabla^2 - Z_A/r_A + J_A - K_A - Z_B/r_B + J_B - K_B \quad (II-2)$$

where the Coulomb and exchange operators associated with center A are defined by

$$J_A \phi(1) = \sum_i q_i \langle \phi_i | r_{12}^{-1} | \phi_i \rangle \phi(1) \quad (II-3)$$

and

$$K_A \phi(1) = \sum_i q_i \langle \phi_i | r_{12}^{-1} | \phi_i \rangle \phi_i(1) \quad (II-4)$$

where the Dirac brackets here denote integration over the coordinates of electron 2 and summation over its spin. The  $q_i$ 's are the spin-orbital occupation numbers. Analogous definitions for the Coulomb and exchange operators on atom B are assumed. The spin-orbitals are not restricted to be eigensolutions to a pseudoeigenvalue problem,

$$F_1 \phi(1) = \epsilon \phi(1), \quad (II-5)$$

although they must be solved for self-consistently since the operator depends on them through the Coulomb and exchange operators.

At this point we have done nothing but invoke the Hartree-Fock approximation with the only twist being the localized restriction on the spin-orbitals. The canonical Hartree-Fock scheme would require that the spin-orbitals be symmetry-adapted, that is, invariant (except possibly a change in sign) under the operations of the molecular symmetry point group. This, of course, is an unnecessary, but convenient, restriction. Only the total state need be invariant, and such invariance can be achieved with equivalent orbitals (Hurley et al., 1953), which transform into each other under the operations of the group. Such orbitals are more general and can usually be well-localized. We shall use such localized equivalent orbitals in our treatment and restrict, instead, our spin-orbitals to be centered on a single atomic site. So each "molecular" spin-orbital will be associated unambiguously to a specific atom.

We wish now to simulate an atom-in-molecule partitioning of the pseudoeigenvalue problem in (II-5). To effect the partitioning, let us look at the diatomic molecule A-B at very large interatomic separation where the fifth and sixth terms in (II-1) become negligible and the eigenfunctions of  $F$  in (II-2) approach the atomic canonical Hartree-Fock spin-orbitals associated with the two eigenvalue problems

$$F \phi_i^A [C] = \left\{ -\frac{1}{2} \nabla^2 - \frac{Z_A}{r_A} + J[C] - K[C] \right\} \phi_i^A [0] \quad (\text{II-6})$$

and



$$F \phi_i^{(B)} [C] = \left\{ -1/2 \nabla^2 - \sum_{1B} \frac{1}{r} + J [C] - K [0] \right\} \phi_i^{(B)} [0] \quad (II-7)$$

where the [0] denotes this separated-atom case (dropping the reference to electron 1 on the operators and the functions). It should be emphasized that this limiting feature is a consequence of the localized form which we have chosen and that the canonical molecular orbitals would have separated rather unpredictably (particularly where high symmetry exists). Now as we allow the two atoms to approach each other and interact, let us focus our attention on a specific atom, say A. Suppose that instead of solving (II-2) for all of its eigenfunctions, we seek only those solutions which we associate with atom A, while the solutions of (II-7) for atom B are assumed to suffice, for the moment, as the solutions of (II-2) associated with atom B. That is, we wish to solve the pseudoeigenvalue problem

$$F \phi_i^{(A)} [1] = \left\{ -1/2 \nabla^2 - \sum_{1A} \frac{1}{r} + J [1] - K [1] - \sum_{1B} \frac{1}{r} + J [C] - K [0] \right\} \phi_i^{(A)} [1] \quad (II-8)$$

for all the functions centered on A, while holding the functions on B fixed as though they were already self-consistent eigenfunctions of F in (II-2). The [1] here denotes the first iterate of this higher-level self-consistent process. In order for the functions on both centers A and B to be simultaneous eigenfunctions of F, they must be noninteracting through F, that is,

$$\langle \phi_i^A [1] | \phi_j^B [0] \rangle = 0, \quad \forall i, j \quad (\text{II-9})$$

must be satisfied. It is sufficient, though, that they be orthogonal,

$$\langle \phi_i^A [1] | \phi_j^B [0] \rangle = 0, \quad \forall i, j, \quad (\text{II-10})$$

if either is in fact an eigenfunction. But before we treat this restriction on the eigenvalue problem, let us follow through with our proposition a little further.

We obviously could have just as easily chosen to concentrate on atom B and ended up with the eigenvalue problem

$$\begin{aligned} E \phi_j^B [1] = & \left[ -1/2 \nabla^2 - \frac{Z}{r_B} + J [1] - K [1] \right. \\ & \left. - \frac{Z}{r_A} + J [0] - K [0] \right] \phi_j^B [1] \end{aligned} \quad (\text{II-11})$$

subject to the constraints

$$\langle \phi_i^A [0] | \phi_j^B [1] \rangle = 0, \quad \forall i, j. \quad (\text{II-12})$$

This would give us a full set of functions,  $\phi[1]$ 's, corresponding to our first level of iteration. It is fairly easy to see how one could continue this reasoning to obtain a set of  $\phi[2]$ 's from the  $\phi[1]$ 's, and so on, until some degree of convergence is attained, that is, until

$$\phi_i^A [n] \rightarrow \phi_i^A [n-1],$$

$$\phi_j^B [n] \rightarrow \phi_j^B [n-1], \quad (\text{II-13})$$

and we satisfy the orthogonality conditions

$$\langle \phi_i^A [n] | \phi_j^B [n] \rangle = 0, \quad \forall i, j. \quad (\text{II-14})$$

Getting back now to the problem of handling the additional constraints on the pseudoeigenvalue problem, we intend to treat this problem with the projection operator technique (Löwdin, 1961). The preceding development and much of what is about to follow could just as well have been treated with partitioning technique (Löwdin, 1964), but we shall dispense with this equivalent approach for the time being. Let us start by considering a general unconstrained function whose projection is the desired function,

$$\begin{aligned} \phi_i^A &= \bar{\phi}_i^A - \sum_j^{(B)} \langle \phi_j^B | \phi_i^A \rangle \phi_j^B \\ &= (1-P)_B \bar{\phi}_i^A \end{aligned} \quad (\text{II-15})$$

where

$$P = P_E = \sum_j^{(E)} |\phi_j^E \rangle \langle \phi_j^E| \quad (\text{II-16})$$

is the projection operator which projects out the "B-part" of the functions on A. Condition (II-14) in terms of the

unconstrained functions (dropping now the [n]-notation at self-consistency) becomes automatically satisfied,

$$\begin{aligned}
 \langle \bar{\phi}_i^A | F | \bar{\phi}_j^B \rangle &= \langle \bar{\phi}_i^A | (1-P)_B | \bar{\phi}_j^B \rangle \\
 &= \langle \bar{\phi}_i^A | F | \bar{\phi}_j^B \rangle - \langle \bar{\phi}_i^A | P | \bar{\phi}_j^B \rangle \\
 &= \epsilon_{ij} \langle \bar{\phi}_i^A | \bar{\phi}_j^B \rangle - \sum_k \epsilon_{kj} \langle \bar{\phi}_i^A | \bar{\phi}_k^B \rangle \langle \bar{\phi}_k^B | \bar{\phi}_j^B \rangle \\
 &= 0
 \end{aligned} \tag{II-17}$$

where we have made use of the fact that the functions on center B are eigenfunctions of F and thus orthogonal amongst themselves. The eigenvalue problem associated with atom A in terms of these unconstrained functions would be

$$F \frac{\bar{\phi}_i^A}{E} = \epsilon \frac{\bar{\phi}_i^A}{E} (1-P)_B \frac{\bar{\phi}_i^A}{E}, \tag{II-18}$$

and the secular problem would then become

$$|\langle \bar{\phi}_i^A | (1-P)_B (E-\epsilon) (1-P)_B | \bar{\phi}_j^A \rangle| = 0. \tag{II-19}$$

Thus, we have transferred the restriction on the eigenfunctions to a modification of the operator. We therefore seek instead the unconstrained solutions to a projected Hamiltonian. The analogous secular problem associated with atom B would be

$$|\langle \bar{\phi}_i^B | (1-P)_A (E-\epsilon) (1-P)_A | \bar{\phi}_j^B \rangle| = 0 \tag{II-20}$$

with analogous definitions for the unconstrained functions on atom B and for the projection operator associated with the "A-part" of A-B.

If we rewrite equations (II-19) and (II-20) with the unprojected operator F separated out, we get (Weeks et al., 1969)

$$|\langle \phi_i^A | F + V_A - \epsilon | \phi_j^A \rangle| = C \quad (\text{II-21})$$

and

$$|\langle \phi_i^B | F + V_B - \epsilon | \phi_j^B \rangle| = C \quad (\text{II-22})$$

where the pseudopotentials are given by

$$V_A = -(P_A F - \epsilon P_A) (2 - P_A) - [F, P_A] \quad (\text{II-23})$$

and

$$V_B = -(P_B F - \epsilon P_B) (2 - P_B) - [F, P_B]. \quad (\text{II-24})$$

It should be noted that the second term in (II-23) and (II-24) will vanish if the operator F commutes with the projector operators, that is,

$$[F, P_A] = [F, P_B] = 0. \quad (\text{II-25})$$

Furthermore, if the "projection" operators are truly idempotent, then these pseudopotentials reduce to

$$V_A = -(F - \epsilon) P_A \quad (\text{II-26})$$

and

$$V_B = -(F - \epsilon) P_B. \quad (\text{II-27})$$

As the problem has been formulated so far, both of these requirements are fulfilled, but these terms shall be retained for reasons which will be clarified later.

At this point the diatomic problem has been effectively reduced to two coupled atomic problems without any serious approximations outside the independent-particle model or limitations imposed on the basis, but, we still have not really simplified the problem with respect to size or effort either. We have merely reformulated the problem to prompt new insight. The fact that we have not yet gained anything is evident when we realize that the Coulomb, exchange and projection operators are all defined in terms of the constrained functions and that the unconstrained functions are neither eigenfunctions of  $F$  nor orthonormal. Although the unconstrained eigenfunctions of our modified operators

$$(F+V)_A \bar{\phi}_i^A = \epsilon_i^A \phi_i^A \quad (\text{II-28})$$

$$(F+V)_B \bar{\phi}_j^B = \epsilon_j^B \phi_j^B \quad (\text{II-29})$$

share a common set of eigenvalues with the constrained eigenfunctions of  $F$  (Weeks et al., 1969), they are not simultaneous eigenfunctions of the same operator. Since the eigenfunctions on different centers correspond to different operators, they need not be orthogonal. In fact, because of the energy dependence of the pseudopotentials, all the

eigenfunctions should, in principle, correspond to different operators. This energy dependence of the pseudopotentials will be taken up in the next chapter.

In principle, one could solve directly for the unconstrained eigenfunctions of the modified operator and then regenerate the constrained eigenfunctions of  $F$ , from which one could obtain new Coulomb, exchange and projection operators (and a total energy). However, this reintroduces multicenter additions to our otherwise single-center unconstrained functions, and thus multicenter integrals, which is precisely what we have set out to avoid. This brings us to our first major approximation.

In the beginning, we assumed that each spin-orbital could be unambiguously assigned to a particular atom and, more importantly, expanded in a single-center basis. Our unconstrained eigenfunctions have this property imposed on them directly by limiting the basis in the solution of the projected eigenvalue problem. However, as we have just noted above, this indirectly forces the constrained eigenfunctions of the unprojected eigenvalue problem to deviate from this distinction. Before making any more assumptions about the individual spin-orbitals, we must recall that the only thing which has any direct consequence is the form of the total density itself,

$$\sum_i^{(A)} \phi_i^* \phi_i, \quad (II-30)$$

which occurs in the Coulomb and exchange operators, the projection operators, and the total energy expression. In terms of the unconstrained functions the total density may be written

$$\sum_i^{(A)} (1-P)_B \phi_i^* (1-P)_B \phi_i, \quad (II-31)$$

which upon expansion of the projection operators gives

$$\begin{aligned} \sum_i^{(A)} \phi_i^* \phi_i &= \sum_i^{(A)} \sum_j^{(B)} \langle \phi_i | \phi_j \rangle \phi_j^* \phi_i \\ &- \sum_i^{(A)} \sum_j^{(B)} \langle \phi_j | \phi_i \rangle \phi_i^* \phi_j \\ &+ \sum_i^{(A)} \sum_{j,k}^{(B)} \langle \phi_i | \phi_j \rangle \langle \phi_j | \phi_k \rangle \phi_i^* \phi_k. \end{aligned} \quad (II-32)$$

If we now invoke the Mulliken approximation (1949) for the differential overlap,

$$\phi_i^* \phi_j = \langle \phi_i | \phi_j \rangle (\phi_i^* \phi_i + \phi_j^* \phi_j) / 2, \quad (II-33)$$

then (II-31) becomes



$$\begin{aligned}
 \sum_i (A) \frac{\bar{A}^* \bar{A}}{\phi_i \phi_i} - \sum_i (A) \sum_j (B) \frac{\bar{A} \bar{B}^2 \bar{A}^* \bar{A}}{\langle \phi_i | \phi_j \rangle (\phi_i \phi_i + \phi_j \phi_j)} + \sum_j (B) \frac{\bar{B}^* \bar{B}}{\phi_j \phi_j} \\
 + \sum_i (A) \sum_j (B) \frac{\bar{A} \bar{B}^2 \bar{B}^* \bar{B}}{\langle \phi_i | \phi_j \rangle \phi_j \phi_j} \\
 = \sum_i (A) \left( 1 - \sum_j (B) \frac{\bar{A} \bar{B}^2}{\langle \phi_i | \phi_j \rangle} \right) \frac{\bar{A}^* \bar{A}}{\phi_i \phi_i} \\
 = \sum_i (A) \frac{\bar{A}^* \bar{A}}{\phi_i \phi_i} \quad (II-34)
 \end{aligned}$$

where

$$\frac{\bar{A}}{\phi_i} = \left( 1 - \sum_j (B) \frac{\bar{A} \bar{B}^2}{\langle \phi_i | \phi_j \rangle} \right)^{-1/2} \frac{\bar{A}}{\phi_i} \quad (II-35)$$

and

$$\langle \frac{\bar{A}}{\phi_i} | \frac{\bar{A}}{\phi_i} \rangle = 1. \quad (II-36)$$

Thus, the Mulliken approximation leads directly to a form of the total density in terms of the single-center unconstrained functions which have been renormalized to unity. So with this as an incentive, we shall replace the constrained functions, wherever they occur, by their renormalized unconstrained counterparts, that is,

$$\frac{\bar{A}}{\phi_i} = \frac{\bar{A}}{\phi_i}. \quad (II-37)$$

We will drop the "prime" notation and keep in mind that this substitution shall always be in effect. The full impact of retaining the localized single-center expansions will not be realized until approximate forms for the interatomic interactions are introduced in chapters IV and V.

Before looking in more detail at the pseudopotentials, let us consider what additional problems we can expect when the same reasoning is extended to molecules beyond diatomics. In brief, the secular problem, analogous to (II-19), that would be associated with atom A in the triatomic molecule A-B-E' is

$$|\langle \bar{\phi}_i^A | (1-P_B) (1-P_{B'}) (E-E) (1-E_{B'}) (1-P_B) | \bar{\phi}_j^A \rangle| = 0 \quad (II-38)$$

where now, in general, the projection operators are not orthogonal (or disjoint), that is,

$$P_B P_{B'} \phi_j(1) = \sum_j^{(E)} \sum_k^{(E')} \langle \phi_j | \phi_k \rangle \langle \phi_k | \phi_j \rangle \phi_j(1) \quad (II-39)$$

where

$$\langle \phi_j^E | \phi_k^{E'} \rangle \neq 0. \quad (II-40)$$

We would get analogous expressions for atoms B and B'. The corresponding pseudopotentials would thus be more complicated than those encountered in the diatomic case, unless some simplifying assumptions can be made. An attempt will be made in the next chapter to retain a pseudopotential which is accurate to at least second-order in interatomic overlap. This next chapter is devoted to a more detailed look at the pseudopotentials, with particular attention paid to the energy dependence.

CHAPTER III  
THE ENERGY-DEPENDENT PSEUDOPOTENTIAL

In the previous chapter, we have essentially defined an effective atom-in-molecule one-electron Hamiltonian. Its associated eigenvalue problem has the form as that

$$Q F Q \phi = \epsilon \phi \quad (\text{III-1})$$

where  $F$  is the polyatomic analog of (II-2) and  $Q$  is a product of projection operators,

$$Q = (1 - P_B)(1 - P_{B'}) (1 - P_{B''}) \dots, \quad (\text{III-2})$$

which are not in general disjoint (and so  $Q$  is not in general a projection operator itself). If we expand  $Q$ ,

$$Q = 1 - P_B - P_{B'} - \dots + P_B P_{B'} + P_B P_{B''} + \dots, \quad (\text{III-3})$$

and retain only terms up to second-order in differential overlap (second-order in  $P$ ), and then invoke the Mulliken approximation (1949) for the terms involving interatomic differential overlap,

$$\langle \phi_i^B | \phi_j^{B'} \rangle = 1/2 \langle \phi_i^B | \phi_j^{B'} \rangle (\langle \phi_i^B | \phi_i^B \rangle + \langle \phi_j^{B'} | \phi_j^{B'} \rangle), \quad (\text{III-4})$$

we get the general form for  $Q$

$$Q = 1 - P \quad (\text{III-5})$$

where

$$P = \sum_i^{(E)} \left( 1 - \sum_{j \neq i}^{(B')} \frac{B_i B_j}{\langle \phi_i | \phi_j \rangle} \right) |\phi_i\rangle \langle \phi_i| \quad (\text{III-6})$$

The first sum in (III-6) is over all normalized (nonorthogonal) unconstrained eigenfunctions associated with all the atoms (B) in the molecule except the one with which Q is associated (A), and the second inner sum is over all atoms except A and the particular atom B being summed over in the outer sum. The operator P thus "projects" out the space complementary to the atom being considered (A), which is just a generalization of the projection operators we encountered for the diatomic case in the previous chapter, that is,

$$P = P^+ = \sum_i^{(B)} \frac{B_i B_i}{\langle \phi_i | \phi_i \rangle} |\phi_i\rangle \langle \phi_i| \quad (\text{III-7})$$

with

$$Y_i = 1 - \sum_{j \neq i}^{(B')} \frac{B_i B_j}{\langle \phi_i | \phi_j \rangle} \quad (\text{III-8})$$

being an overlap correction to the "projection" manifold. In the limit of zero-overlap, P is a true projection operator with the idempency relation fulfilled.

The secular problem which we then wish to solve is of the same form as (II-19), namely

$$|\langle \phi_i | (1-P)^\dagger (F-E) (1-P) | \phi_j \rangle| = 0 \quad (\text{III-9})$$

or in terms of a pseudopotential

$$|\langle \phi_i | F+V-E | \phi_j \rangle| = 0 \quad (\text{III-10})$$

where, analogous to (II-23),

$$V = -(FF-EI) (2-P) - [F,P]. \quad (\text{III-11})$$

In order to simplify the form of V, as in (II-26), we need to examine FP and PF in some detail. Let us first consider the former,

$$FP = F \sum_i^{(B)} \gamma_i^B |\phi_i\rangle \langle \phi_i|. \quad (\text{III-12})$$

We must recall that the eigenfunctions in (III-12) are not eigenfunctions of F but rather

$$(F+V) \phi_i^B = \epsilon_i^B \phi_i^B \quad (\text{III-13})$$

with the corresponding pseudopotential associated with the environment of atom B. Rearranging (III-13) gives

$$F \phi_i^B = \epsilon_i^B \phi_i^B - V \phi_i^B \quad (\text{III-14})$$

which through first-order in perturbation theory becomes

$$F \phi_i^B = \bar{\epsilon}_i^B \phi_i^B \quad (\text{III-15})$$

where

$$\bar{\epsilon}_i^B = \epsilon_i^B - \langle \phi_i^B | V | \phi_i^B \rangle. \quad (\text{III-16})$$

Using this now in (III-12) gives

$$FF = \sum_i^{(B)} \frac{-E}{\epsilon} \frac{B}{i} \frac{B}{i} \frac{E}{i} \frac{B}{i} |\phi\rangle \langle \phi| \quad (III-17)$$

and since F is a self-adjoint operator, (III-15) also grants

$$FF = FF \quad (III-18)$$

causing the commutator in (III-11) to vanish, leaving us with

$$V = -(F-\epsilon)(2P-PP). \quad (III-19)$$

Looking now at FF we have that

$$FF = \sum_i^{(B)} \sum_j^{(B')} \frac{E}{i} \frac{B}{i} \frac{B'}{j} \frac{B}{i} \frac{E}{i} \frac{B'}{j} \frac{B'}{j} |\phi\rangle \langle \phi| \quad (III-20)$$

If we again invoke Mulliken's approximation (III-4) then

$$FF = \sum_i^{(B)} \frac{-E}{\epsilon} \frac{E}{i} \frac{B}{i} \frac{B}{i} |\phi\rangle \langle \phi| \quad (III-21)$$

where

$$\frac{-E}{\epsilon} = \frac{E}{i} + \sum_{j \neq i}^{(B')} \frac{E'}{j} \frac{B}{i} \frac{B'}{j} \quad (III-22)$$

Substituting (III-17) and (III-21) into (III-19) we obtain

$$V = \sum_i^{(E)} (\epsilon - \frac{-E}{\epsilon}) (2 - \frac{-E}{\epsilon}) \frac{E}{i} \frac{B}{i} \frac{B}{i} \frac{E}{i} |\phi\rangle \langle \phi| \quad (III-23)$$

which in the limit of an orthonormal "projection" manifold

reduces to the Phillips-Kleinman (1959) pseudopotential

$$V = \sum_i^{(E)} (\epsilon - \frac{E}{i}) \frac{E}{i} \frac{B}{i} \frac{B}{i} |\phi\rangle \langle \phi|. \quad (III-24)$$

One should note the explicit dependence of V on the energy eigenvalue  $\epsilon$ . This energy dependence is the only remaining complication in writing down the final matrix

equations for solving the secular problem in (III-10). Before getting into the energy dependence, though, let us introduce a basis and proceed to set up these matrix equations.

For the sake of clarity and simplicity, we consider an orthonormal basis centered on the atom (A) with which we are currently concerned, such that

$$\phi_i = \sum_{k=1}^M u_{ki} C_k \quad (\text{III-25})$$

or in matrix notation

$$\phi = u C \quad (\text{III-26})$$

where M is the number of functions in the basis (and so the maximum number of eigenfunctions we can obtain). We then consider a composite basis for all the other eigenfunctions centered on their respective atomic centers, that is,

$$\psi_i = \sum_k \begin{pmatrix} E \\ B \end{pmatrix} u_{ki} C_k \quad (\text{III-27})$$

or in matrix notation

$$\psi = u C \quad (\text{III-28})$$

If we now define the matrices

$$S_{kl} = \langle u_k | u_l \rangle, \quad (\text{III-29})$$

$$P_{kl} = \sum_i \begin{pmatrix} B \\ B^* \end{pmatrix} (2-\delta_{ij}) \gamma_{ij} C_k C_l \quad (\text{III-30})$$

and

$$R_{kl} = \sum_i \begin{matrix} (B) & \bar{B} & & & & \\ & \varepsilon & (2-\gamma) & \gamma & C & C \\ & & i & i & k_i & l_i \end{matrix} \quad \text{(III-31)}$$

then

$$\begin{aligned} V_{kl} &= \langle u_k | V | u_l \rangle \\ &= \varepsilon (SFS)_{kl}^+ - (SRS)_{kl}^+ \end{aligned} \quad \text{(III-32)}$$

Thus, aside from the energy dependence of  $V$ , the secular problem (III-10) reduces to finding the unitary matrix  $C$  such that

$$C^+ (F+V)C = \varepsilon \quad \text{(III-33)}$$

where

$$F_{kl} = \langle u_k | F | u_l \rangle \quad \text{(III-34)}$$

and  $\varepsilon$  is now a diagonal matrix.

As already stated, the only remaining complication is the explicit energy dependence of the pseudopotential (III-32). As long as this energy dependence is there, we can not seek simultaneous eigenfunctions of the same operator, since each eigenfunction would correspond to a different operator dependent upon its own eigenvalue. Such eigenfunctions would not even be orthogonal to each other. Operators of this nature, which correspond to a one-dimensional Hilbert space, are also inherently non-Hermitian in any matrix representation (of order higher than one). We shall now



derive an approximate form for the pseudopotential which is explicitly energy independent and Hermitean. First, let us rewrite (III-33) in terms of a modified Fock matrix, that is,

$$C^+ \bar{F} C = \epsilon \quad (\text{III-35})$$

where

$$\bar{F} = F + \epsilon \bar{P} - \bar{R}, \quad (\text{III-36})$$

$$\bar{P} = S^+ F S, \quad (\text{III-37})$$

and

$$\bar{R} = S^+ B S. \quad (\text{III-38})$$

Then we note that from (III-35)

$$\bar{F} C = C \epsilon. \quad (\text{III-39})$$

Now putting (III-36) back into (III-35) we have

$$C^+ F C + C^+ \bar{P} C \epsilon - C^+ \bar{R} C = \epsilon \quad (\text{III-40})$$

which upon substitution of (III-39) becomes

$$C^+ F C + C^+ \bar{P} F C - C^+ \bar{R} C = \epsilon \quad (\text{III-41})$$

or

$$C^+ (F + \bar{P} F - \bar{R}) C = \epsilon. \quad (\text{III-42})$$

So comparing this with (III-35) we have that

$$\bar{F} = F + \bar{P} F - \bar{R} \quad (\text{III-43})$$

which upon rearranging gives

$$\bar{F} = (1 - \bar{P})^{-1} (F - \bar{R}). \quad (\text{III-44})$$

If we now expand the inverse, we generate the series

$$\bar{F} = F - \bar{F} + \bar{P}F - \bar{P}\bar{F} + \bar{P}\bar{P}F - \dots \quad (\text{III-45})$$

from which, along with (III-36) and (III-43), we gather that

$$\bar{\epsilon}P = \bar{F}\bar{F} = \bar{F}F - \bar{F}\bar{R} + \bar{P}F - \dots \quad (\text{III-46})$$

which is similar to a perturbation expansion. Since the pseudopotential matrices (III-37, III-38) are already second-order in overlap, this series should be rapidly convergent. In fact, we shall take only the first two terms of (III-46) in our approximation. The non-Hermiticity is also apparent in this expansion form, and so we choose the approximate Hermitean form for (III-46)

$$\bar{\epsilon}P = (\bar{F}F - \bar{P}\bar{F} + \bar{P}F - \bar{R}\bar{F}) / 2. \quad (\text{III-47})$$

Our modified Fock matrix then becomes

$$\bar{F} = F - \bar{F} + (\bar{F}F - \bar{R}\bar{F} + \bar{P}F - \bar{R}\bar{F}) / 2. \quad (\text{III-48})$$

We have at this point arrived at a scheme for treating a specific atom within a polyatomic system. This scheme can be used for each atom in the system, which are then coupled in a self-consistent manner as described in the previous chapter. All aspects of the Hartree-Fock scheme (or any generalization of this independent-particle model) have been preserved, with the environment of each atom being reduced to the inclusion of additional potential terms. Our largest sacrifice was made in return for the one-center expansion of

the eigenfunctions; however, we have not yet used this to its full advantage. Although we have eliminated all three- and four-center two-electron integrals and many two-center integrals, we have only replaced them by just as many one- and two-center integrals. This reduction alone may very well have been worth the sacrifice, but the goal here is for a more substantial reduction in work. The localized picture which comes out of this projected Hamiltonian approach can be used to its fullest advantage in approximating the interatomic Coulombic and exchange interactions which now have their closest resemblance to an electrostatic model. This will be the topic of the next two chapters.

## CHAPTER IV

### A MODEL APPROXIMATION TO THE EFFECTIVE ONE-ELECTRON INTERATOMIC COULOMB POTENTIAL

If one can substantially reduce the number of multicenter two-electron integrals encountered in conventional analytic ab initio methods, the computational savings would be overwhelming. In the last chapter, the multicenter integrals were all reduced to at most two-center integrals by restricting the eigenfunctions to one-center expansions. The actual number of integrals, however, has not been changed. We shall in this chapter exploit the localized picture and substantially reduce the number of two-center Coulomb integrals. This shall be done by replacing the effective one-electron operator, for the two-electron Coulomb interaction, by a model approximation.

The integrals which we wish to approximate are of the form

$$\langle \phi_i | J | \phi_i \rangle^E \quad (IV-1)$$

which is the Coulombic interaction of the  $i$ -th spin-orbital with all the other spin-orbitals in the polyatomic system except those on the same atomic center (A). The effective one-electron operator is given more explicitly by

$$J = \sum_{j=1}^{E-1} q_j \langle \phi_j | r_{12}^{-1} | \phi_j \rangle \quad (\text{IV-2})$$

where the  $q$ 's are spin-orbital occupation numbers and the subscript 1 is used (but dropped from here on) to emphasize the functional dependence of the operator  $J$  on the coordinates of electron 1. When the eigenfunctions are expanded in a basis, one generates the multitude of multicenter two-electron integrals of the type

$$\langle u_k u_m | r_{12}^{-1} | u_l u_n \rangle. \quad (\text{IV-3})$$

It is the intricate dependence of  $J$  on the coordinates of electron 1 that does not allow for a simpler treatment of this operator, and so we seek an analytic function with a simpler functional dependence to approximate the operator  $J$ .

Let us restrict ourselves to the case of a diatomic molecule for the moment, where  $J$  is centered on a single atom (B). Then for large interatomic separation  $J$  approaches the approximate form

$$J = N \frac{E-1}{1B} \quad (\text{IV-4})$$

where the total electronic charge is reduced to a point charge on the distant atomic center. This corresponds to replacing the electronic coordinates of electron 2 in (IV-2) by the nuclear coordinates of atom B, that is,

$$J = \sum_i^{(B)} q_i \langle \Phi | r_i^{-1} | \Phi \rangle. \quad (IV-5)$$

At lesser interatomic separation, where the charge density can no longer be considered a point charge, the interelectronic distance must undergo an effective dilation to account for the more diffuse charge. Furthermore, as electron 1 approaches the nucleus of atom B, the nuclear attraction should not witness any appreciable screening, and therefore any model function should go to zero as this distance goes to zero. The following model potential function, which we now choose, has these desired properties:

$$J = K \left[ 1 - \chi \left( \frac{r}{r_B} \right) \right] r_B^{-1} \quad (IV-6)$$

where  $\chi$  is a screening function with the asymptotic behavior

$$\chi(0) = 1 \quad (IV-7)$$

and

$$\chi(\infty) = 0. \quad (IV-8)$$

Such a screening function is inherent to the Thomas-Fermi model (Thomas, 1928; Fermi, 1928) of the atom. A significant feature of the Thomas-Fermi screening function is that it is universal for all neutral atoms with respect to the dimensionless variable

$$x_{1B} = r \left[ \frac{2}{3} \frac{Z}{r} \right]^{-1/3} \quad (IV-9)$$

in terms of the nuclear charge. The distance  $r$  is assumed to be given in Bohrs. Potentials of the form (IV-6) are certainly nothing new and most such potentials (Hellman, 1935) adopt an exponential behavior for the screening function  $X$ . We make the choice

$$X_{1B}(r) = \sum_{t} A_{t} X_{1B}(n, l, m, a; r) \quad (IV-10)$$

where

$$X_{1B}(n, l, m, a; r) = r^{n-1} \exp(-ax) Y_{lm}(\theta, \phi) \quad (IV-11)$$

and where the exponential factors are, in principle, universal and could be used for all atoms (with the appropriate change in  $x$ ). Any angular distortions are taken into account with the real normalized spherical harmonics. The linear coefficients are to be determined by fitting the approximate form of  $J$  in (IV-6) to its true form in (IV-5) along with the constraint in (IV-7). We have merely expanded the operator  $J$  in a basis of Slater-type functions (with a somewhat universal choice of exponents).

The linear coefficients are computationally quite simple to handle since they can be taken outside the integrals in which they appear. The coefficients can be determined by substituting (IV-6) for (IV-5) in the one-center Coulomb

integrals occurring on atom B and matching their values, that is,

$$\langle \phi_i^E | \bar{J} | \phi_i^E \rangle = \langle \phi_i^B | J | \phi_i^B \rangle \quad (IV-12)$$

for each eigenfunction on atom B. In more detail we have

$$\begin{aligned} N \left[ \langle \phi_i^E | r | \phi_i^E \rangle - \sum_t A_{tE} \langle \phi_i^E | X(r) | \phi_i^E \rangle \right] \\ = \sum_j (E)_{jE} \langle \phi_i^E | \phi_j^E | r | \phi_i^E \rangle \end{aligned} \quad (IV-13)$$

where the Coulomb integrals on the righthand side of the equation are one-center integrals which we properly compute and retain. We have as many equations like (IV-13) as there are eigenfunctions on that atom, consequently we can fit up to just as many linear coefficients. The number of terms that are needed in (IV-10), though, are usually much less than that (due to its relatively smooth behavior), so some type of (weighted) least-squares fit procedure should be adequate. One other condition, perhaps even more important, that can be satisfied is the total two-center nuclear attractor experienced by that atom, given by

$$Z \sum_j (E)_{jE} \langle \phi_i^E | r | \phi_i^E \rangle = Z \sum_{BA} J(r_{BA}) \quad (IV-14)$$

In the general case of a polyatomic, this would be a sum over all the other atoms. Thus, in addition to the equations in (IV-13), we can have



$$\begin{aligned}
 N \begin{bmatrix} \tau \\ \tau \\ \vdots \\ \tau \end{bmatrix} &= \sum_{t \in AE} \begin{bmatrix} B & B & \rightarrow & -1 \\ A & X & (\tau) & \tau \\ & & & AB \end{bmatrix} \\
 &= \sum_j \begin{bmatrix} (B) & B & B & -1 & B \\ q & \langle \phi | \tau | \phi \rangle & & 1A & B \end{bmatrix}. \tag{IV-15}
 \end{aligned}$$

In order to determine the linear coefficients, these linear equations can be written in the matrix form

$$T A = G \tag{IV-16}$$

where

$$A = \begin{matrix} E \\ A \\ t \end{matrix}, \tag{IV-17}$$

$$T_{it} = N \begin{bmatrix} B & B & B & \rightarrow & -1 & B \\ \langle \phi | X & (\tau) & \tau & | \phi \rangle & & \\ 1B & & 1B & & & i \end{bmatrix}, \tag{IV-18}$$

$$T_{M+1,t} = N \begin{bmatrix} E & B & \rightarrow & -1 \\ X & (\tau) & \tau & \\ t & AE & AB & \end{bmatrix}, \tag{IV-19}$$

$$\begin{aligned}
 T_{M+2,t} &= 1 \text{ if } \begin{matrix} B \\ l \\ t \end{matrix} = C, \\
 &= 0 \text{ if } \begin{matrix} B \\ l \\ t \end{matrix} > C, \tag{IV-20}
 \end{aligned}$$

$$\begin{aligned}
 G_i &= N \begin{bmatrix} E & B & -1 & E \\ \langle \phi | \tau & | \phi \rangle & & \\ i & 1B & i & \end{bmatrix} \\
 &= \sum_j \begin{bmatrix} (B) & B & B & E & -1 & B & E \\ q & \langle \phi | \phi | \tau & | \phi \phi \rangle & & & & \\ j & j & i & j & 12 & i & j \end{bmatrix}, \tag{IV-21}
 \end{aligned}$$

$$G_{M+1} = N \begin{bmatrix} B & -1 \\ \tau & AB \end{bmatrix} - \sum_j \begin{bmatrix} (B) & B & B & -1 & B \\ q & \langle \phi | \tau & | \phi \rangle & & \\ j & j & j & 1A & j \end{bmatrix}, \tag{IV-22}$$

and

$$G_{M+2} = 1. \tag{IV-23}$$

In general  $M+2$  is larger than the number of terms needed in (IV-10), and so we have an overdetermined set. If  $M+2$  and  $N$  were equal, then  $T$  would be square and

$$A = T^{-1} G, \quad (IV-24)$$

provided that  $T$  is non-singular (no linear dependencies). However, in the general case, one can write the normal set of equations (IV-16) as

$${}^t(T w T) A = (T w) G \quad (IV-25)$$

where  $w$  is an arbitrary diagonal matrix whose elements act as weights to the original  $M+2$  equations (IV-16). The choice of a unit matrix would correspond to the usual linear least-squares fit procedure; nevertheless, the option of giving more importance to certain conditions such as the external nuclear attraction (IV-14,15) or to the valence orbitals over the core orbitals can be useful. Since we now have square matrices, we can solve for  $A$  in terms of the generalized inverse of  $T$ , that is,

$$A = ({}^t(T w T))^{-1} (T w) G. \quad (IV-26)$$

The exponents in (IV-10) could be determined once and for all by a mere fit to the universal Thomas-Fermi screening function mentioned earlier, but this would build in the deficiencies of the Thomas-Fermi model (particularly for small atoms). A better approach, perhaps, was suggested by some work carried out by Csavirszky (1968, 1973). He

performed a variational calculation to determine an analytical solution to the Thomas-Fermi equations with the following trial function for the screening function:

$$\chi(x) = (A'e^{-a'x} + A''e^{-a''x^2}) \quad (IV-27)$$

His calculation yielded the exponents

$$\begin{aligned} a' &= 0.1782559 \quad \text{and} \\ a'' &= 1.759339 \end{aligned} \quad (IV-28)$$

as well as values for  $A'$  and  $A''$  (but these are not of any concern to us). This corresponds to the following choice of exponents in our model potential expression (IV-10):

$$\begin{aligned} a_1 &= 2a' = 0.3565118, \\ a_2 &= a' + a'' = 1.937594, \quad \text{and} \\ a_3 &= 2a'' = 3.518678. \end{aligned} \quad (IV-29)$$

These values were derived for spherically symmetric neutral atoms in the Thomas-Fermi model with somewhat modified boundary conditions implied by the particular choice of (IV-27). In order to allow for corrections to the Thomas-Fermi model, radial and angular distortions, and deviations from neutrality that would exist for an "atom-in-a-molecule", some additional flexibility (other than the variation of the linear coefficients) might be necessary. Augmenting expression (IV-10) with an extra term or two would probably be sufficient for most cases, but angular distortions would certainly necessitate the inclusion of some polarization terms. One could also just choose some

general well-rounded, flexible basis, such as an even-tempered (Bardo and Ruedenberg, 1973) set of exponents, with the hopes that the use of the dimensionless variable  $x$  and well-determined linear coefficients would be sufficient.

CHAPTER V  
AN APPROXIMATE NONLOCAL INTERATOMIC  
EXCHANGE POTENTIAL

In the last chapter, we substantially reduced the number of two-center two-electron Coulomb integrals by exploiting the localized picture. We shall now attempt a similar reduction in the analogous exchange integrals. Again, we wish to approximate the effective one-electron operator, but this time the operator is nonlocal and requires a somewhat different approach.

The two-center exchange integrals are of the form

$$\langle \phi_i | K | \phi_i \rangle \quad (V-1)$$

where  $K$  is the effective nonlocal one-electron operator (subscript 1 dropped from here on) for the exchange interaction with all the other spin-orbitals (of same spin) in the polyatomic system except those associated with this center (A). The operator  $K$  is defined such that

$$K \phi_i = \sum_j \langle \phi_j | r_{12}^{-1} | \phi_i \rangle \phi_j \quad (V-2)$$

Let us consider the asymptotic behaviour of (V-1) when the average interelectronic distance approaches the internuclear distance, that is, when

$$\langle \phi_i^E | K | \phi_i^E \rangle = r^{-1} \sum_{AB} \sum_j q_{ij} \langle \phi_j^B | \phi_j^B \rangle \langle \phi_i^E | \phi_i^E \rangle \quad (V-3)$$

or

$$K_i^E = r^{-1} \sum_{AB} \sum_j q_{ij} \langle \phi_j^B | \phi_j^B \rangle \langle \phi_i^E | \phi_i^E \rangle. \quad (V-4)$$

Since  $K$  is nonlocal, we can no longer use any of its "local" properties, such as its expectation values with respect to the eigenfunctions on its own center, to help determine an intermediate form for its approximation. Our endeavor thus far has been to retain a theory which is valid through at least second-order in diatomic overlap, and so it is felt that retaining  $K$  in its asymptotic form (V-4), which is second-order in overlap, would not be inconsistent with any other approximations made thus far. In such a case, the interatomic exchange can be treated with the same ease as the pseudopotential in chapter III.

This approximation may appear to be a bit crude at first, but the magnitude of these interactions in this localized scheme is relatively small due to the nearly electrostatic nature of the model. It should be emphasized that the approximations used for the interatomic two-electron interactions could only be realized in such a localized separable picture.

CHAPTER VI  
 A MODEL HAMILTONIAN AND AN APPROXIMATE  
 ELECTRON PROPAGATOR

According to the Heisenberg equation of motion for the electron propagator (Linderberg and Öhrn, 1973), in the energy representation, we have in matrix form that

$$\begin{aligned}
 G_{ij}(E) &= \langle\langle a_i; a_j^+ \rangle\rangle_E \\
 &= E^{-1} [\langle\langle a_i, a_j^+ \rangle\rangle + \langle\langle [a_i, H]; a_j^+ \rangle\rangle_E] \quad (\text{VI-1})
 \end{aligned}$$

where

$$\begin{aligned}
 a_i &= \langle\phi | \psi_i \rangle \quad \text{and} \\
 a_i^+ &= \langle\psi_{op} | \phi_i \rangle \quad (\text{VI-2})
 \end{aligned}$$

are the annihilation and creation operators, respectively, with the anticommutation relations

$$\begin{aligned}
 [a_i, a_j^+] &= [a_i^+, a_j^+] = 0 \quad \text{and} \\
 [a_i, a_j^+] &= [a_i^+, a_j^+] = S_{ij} = \langle\phi | \phi_i \phi_j \rangle, \quad (\text{VI-3})
 \end{aligned}$$

defined in terms of field operators and a spin-orbital basis. The many-electron Hamiltonian, in second quantized form, is

$$H = \sum_{ij} h_{ij} a_i^\dagger a_j + 1/2 \sum_{ijkl} (kl|ij) a_i^\dagger a_k^\dagger a_l a_j \quad (VI-4)$$

where

$$h_{ij} = \langle \phi_i | h | \phi_j \rangle \quad (VI-5)$$

and

$$(kl|ij) = \langle \phi_k \phi_l | r_{12}^{-1} | \phi_i \phi_j \rangle \quad (VI-6)$$

are the usual one- and two-electron integrals. Equation (VI-1) can be iterated to yield

$$G_{ij}(E) = E^{-1} S_{ij} + E^{-2} F_{ij} + \dots \quad (VI-7)$$

where

$$F_{ij} = \langle [ [ a_i^\dagger, H ], a_j^\dagger ] \rangle \quad (VI-8)$$

is the first moment and so on. Substituting the Hamiltonian (VI-4) into (VI-8), the first moment becomes

$$F_{ij} = h_{ij} + \sum_{kl} [ (ij|kl) - (il|kj) ] \langle a_k^\dagger a_l \rangle \quad (VI-9)$$

which has the same form as the effective one-electron Hamiltonian as originally presented by Fock (1932) and will henceforth be called the Fock matrix. This more general approach to Hartree-Fock theory will be taken up in the next chapter.



Suppose now that instead of using the correct many-electron Hamiltonian, one substitutes into equation (VI-8) an approximate one-electron model Hamiltonian of the form

$$\bar{H} = \sum_k \varepsilon_k a_k^\dagger a_k = \sum_k \varepsilon_k n_k \quad (\text{VI-10})$$

where the  $n_k$ 's are just the occupation number operators and the  $\varepsilon_k$ 's are real, negative energies of the noninteracting electrons. In our present treatment, we would choose as our spin-orbital basis the nonorthogonal atomic spin-orbitals generated from each projected Hamiltonian calculation, and for the energies we would choose the corresponding eigenvalues, with possible modification (to the positive eigenvalues, for example). The Fock matrix then takes the approximate form

$$\begin{aligned} \bar{F}_{ij} &= \langle [a_i, \bar{H}], a_j^\dagger \rangle \\ &= \sum_k S_{ik} \varepsilon_k S_{kj} \end{aligned} \quad (\text{VI-11})$$

or the matrix form

$$\bar{F} = S \varepsilon S \quad (\text{VI-12})$$

where  $\varepsilon$  is a diagonal matrix. Equation (VI-7) in matrix form becomes

$$\begin{aligned} \bar{G}(E) &= E^{-1} S^{-1} + E^{-2} S \varepsilon S + \dots \\ &= (E S^{-1} - \varepsilon)^{-1} \end{aligned} \quad (\text{VI-13})$$

where one can see that the poles of the propagator will occur at the eigenvalues of the Fock matrix, that is, at the zeros of the secular determinant

$$|S\bar{E}S - F| = 0 \quad (VI-14)$$

The corresponding eigenvalue problem

$$\bar{F}C = SCE \quad (VI-15)$$

can be reduced to the simpler one

$$\bar{F}'C' = C'E \quad (VI-16)$$

where

$$C' C'^{\dagger} = C' C'^{\dagger} = 1 \quad (VI-17)$$

and

$$\bar{F}' = -XSX \quad (VI-18)$$

with X being the diagonal matrix with elements

$$X_{kk} = (-\epsilon_k)^{1/2} \quad (VI-19)$$

This can be considered as the diagonalization of a Fock matrix in a basis which is energy-weighted Löwdin orthogonalized, and this is the reason for the term "Energy-Weighted Maximum Overlap" (EWMO) used by Linderberg et al. (1976) to describe this method. The molecular orbital coefficients in the original basis are given by

$$C_{ki} = C'_{ki} (E_i / \epsilon_k)^{1/2} \quad (VI-20)$$

The electron propagator in this orthogonal basis becomes

$$\bar{G}(E) = X^{-1} (E1 + XSX)^{-1} X S, \quad (VI-21)$$

and the elements of the corresponding one-electron reduced density matrix are given by the contour integral (Linderberg et al., 1976)

$$\begin{aligned}
 \langle a_k^+ a_l \rangle &= (2\pi i)^{-1} \int_C dE \langle \langle a_k^+ ; a_l \rangle \rangle_F \\
 &= (2\pi i)^{-1} \int_C dE \bar{G}_{kl}(E) \\
 &= (2\pi i)^{-1} \int_C dE (X^{-1} (E I + X S X)^{-1} X S)_{kl} \quad (VI-22)
 \end{aligned}$$

where C encloses the occupied energies. An appropriate definition of the charge and bond-order matrix would in this case be

$$P = (2\pi i)^{-1} \int_C dE (E I + X S X)^{-1} \quad (VI-23)$$

This choice leads to

$$q_k = P_{kk} = \sum_i \langle n_i \rangle |C_i^k|^2 \quad (VI-24)$$

for the formal spin-orbital charges in terms of the molecular orbital occupations. This definition is equivalent to the orbital populations according to Mulliken (1955).

In the case of positive energies in (VI-10), one would have to resort to some other type of orthogonal transformation in order to avoid a complex Fock matrix (VI-18). Löwdin's (1970) symmetric orthogonalization

procedure would most closely resemble the procedure just described. The resulting population analysis is, of course, dependent on the type of orthogonal transformation used unless the analysis is done with respect to the original nonorthogonal basis. Population analysis in a nonorthogonal basis, however, can lead to unreasonable charges (negative or greater than one). One could, of course, always solve the complex eigenvalue problem and still use the above procedure, but, in general, the inclusion of positive-energy (virtual) spin-orbitals is not a straightforward task.

CHAPTER VII  
THE GRAND-CANONICAL HARTREE-FOCK SCHEME

The notion of an atom in a molecule led Slater (1970) to consider an energy functional obtained as an average over multiplets arising from a given configuration. His extension of this idea to configurations with fractional occupations, known as the Hyper-Hartree-Fock method, however, has been subject to some criticism because of the appearance of off-diagonal Lagrangian multipliers and lack of certain conceptual grounds (Jørgensen and Øhrn, 1973). In this same spirit we wish to introduce an average based on the statistical mechanical concept of an ensemble (Abdulnur *et al.*, 1972). The particular choice of a Grand Canonical ensemble, as defined by its density operator, leads to the elimination of off-diagonal Lagrangian multipliers.

A system of noninteracting electrons described by the Hamiltonian

$$H = \sum_i \epsilon_i n_i \quad (\text{VII-1})$$

can be described by the Grand Canonical partition function related to the density operator

$$\rho = \prod_i (1 - n_i + z n_i) / (1 + z_i) \quad (\text{VII-2})$$

where

$$z_i = \exp[-(\epsilon_i - \mu) / T]. \quad (\text{VII-3})$$

The parameters  $\mu$  and  $T$  are the thermodynamic chemical potential and absolute temperature. The average value of an operator  $A$  for such a system is then given in terms of its trace with respect to the density operator, that is,

$$\langle A \rangle = \text{Tr} \{ A \rho \}. \quad (\text{VII-4})$$

In particular, the average value of the number operator is

$$\langle n_i \rangle = z_i / (1 + z_i). \quad (\text{VII-5})$$

Using this in expression (VII-2) gives a unique way of defining the density operator from a given set of occupation numbers,

$$\rho = \prod_i [1 - \langle n_i \rangle + (2 \langle n_i \rangle - 1) n_i], \quad (\text{VII-6})$$

without any reference to any thermodynamic parameters. Although there is no connection with equilibrium situations in statistical mechanics, we shall refer to this as a Grand-Canonical density operator, which acts as a formal device for the formation of averages only. Except for the case of all integral occupation numbers, this form of the density operator gives a nonzero width (uncertainty) for the total number operator.

If one considers an electron-conserving (Canonical) average value of the many-electron Hamiltonian in the orthonormal basis which diagonalizes the density matrix, one has

$$\langle H \rangle = \sum_i h_i \langle n_i \rangle + 1/2 \sum_{ij} (J_{ij} - K_{ij}) \langle n_i n_j \rangle \quad (\text{VII-7})$$

where the only thing which is not explicitly determined is the average of the number operator product in the second term. If, however, the average is performed with respect to the Grand-Canonical density operator then

$$\langle n_i n_j \rangle = \langle n_i \rangle \langle n_j \rangle, \quad (\text{VII-8})$$

and equation (VII-3) can be written

$$\langle H \rangle = \sum_i \epsilon_i \langle n_i \rangle - 1/2 \sum_{ij} V_{ij} \langle n_i \rangle \langle n_j \rangle \quad (\text{VII-9})$$

where the effective one-electron energy is given by

$$\epsilon_i = h_i + \sum_j V_{ij} \langle n_j \rangle \quad (\text{VII-10})$$

and the effective interaction energy by

$$V_{ij} = J_{ij} - K_{ij}. \quad (\text{VII-11})$$

One recognizes that these energies can be interpreted as the first and second partial derivatives of the total energy functional  $\langle H \rangle$  with respect to the occupation numbers as follows:

$$\partial \langle H \rangle / \partial \langle n_i \rangle = \epsilon_i \quad (\text{VII-12})$$

and

$$\frac{\partial^2 \langle H \rangle}{\partial \langle n_i \rangle \partial \langle n_j \rangle} = \frac{\partial \epsilon_i}{\partial \langle n_i \rangle} = v_{ij} \quad (\text{VII-13})$$

Such interpretations lead to the finite-difference approximations to ionization energies

$$\Delta E^{(i)} = \epsilon_i \Delta \langle n_i \rangle \quad (\text{VII-14})$$

and excitation energies

$$\Delta E^{(i \rightarrow j)} = \epsilon_i \Delta \langle n_i \rangle + \epsilon_j \Delta \langle n_j \rangle + v_{ij} \Delta \langle n_i \rangle \Delta \langle n_j \rangle \quad (\text{VII-15})$$

for which Kocpmans' (1935) theorem is a special case. Application of the mean value theorem suggests that the best approximations to these quantities would be obtained by determining the  $\epsilon$ 's and  $v$ 's at some intermediate point, such as  $\langle n \rangle = 1/2$ . Such a scheme has been termed the transition state method (Slater and Wood, 1971) when applied to similar energy functionals.

The effective one-electron (Grand-Canonical) operator having these one-electron energies as its eigenvalues, has matrix elements, in an arbitrary nonorthogonal basis, of the form

$$F_{kl} = h_{kl} + \sum_{k'l'} [f(kl|k'l') - (k'l'|k'l)] \langle a_{k'l'}^+ a_{k'l} \rangle \quad (\text{VII-16})$$

where the density matrix elements are given by

$$\langle a_{kl}^+ a_{kl} \rangle = \sum_i C_{li} \langle n_i \rangle C_{ik}^+ \quad (\text{VII-17})$$



and  $C$  is the unitary transformation matrix in this basis which diagonalizes  $F$ , in other words, its columns are the associated eigenvectors of  $F$ . The iterative self-consistent construction and solution of equation (VII-16) is what has come to be called the Grand-Canonical Hartree-Fock (GCHF) method, with the total energy given by equations (VII-9), (VII-10), and (VII-11).

CHAPTER VIII  
A SELF-CONSISTENT CHARGE AND  
CONFIGURATION PROCEDURE

Up to now we have said very little about the manner in which the spin-orbital occupations are assigned. This is somewhat of a sensitive subject, here and in many other "building-block" approaches. This question has its roots in the early days of valence-bond methods.<sup>1</sup> We would like to make an analogy between our method and the single-configuration of nonorthogonal orbitals method.<sup>1</sup> This method amounts to a condensation of many configurations to one, built up from distorted (hybridized) atomic orbitals, which, in essence, is what Coulson and Fischer (1949) did for the hydrogen molecule. The application of this method to larger systems, however, is quite limited because of the difficulty in calculating the matrix elements of the Hamiltonian, since there is no orthogonality between the

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<sup>1</sup>The literature on these methods is just too extensive to review here, but we suggest Gerratt (1974) for an excellent account of the subject as it applies here.

orbitals. The model itself provides a sensible interpretation of chemical bonding in terms of a distortion of the participating atomic orbitals combined with a recoupling of the spins. The method has been shown to be capable of yielding useful estimates of molecular binding energies and other properties. We view our method as a direct means of obtaining such distorted nonorthogonal orbitals, where the orthogonality problem has been incorporated into the pseudopotentials. The renormalized pseudoorbitals (unconstrained functions of chapter II) then act as these hybrid orbitals. The total energy we compute from these orbitals is valid through second-order in overlap (from the Mulliken approximation) and so we should, within the integral approximations made, be able to mimic such a scheme, as far as we can tell. There are some other basic differences, however. These methods generally separate the space and spin parts of their wavefunctions, and consequently couple their spins with proper generalized spin functions.

The concept of "atomic valency" arises when molecules are allowed to separate into their constituent atoms. When the most general linear combination of spin couplings is formed, the resulting separated atomic states can be regarded as well-defined "valence states". Any less coupling, however, can lead to ill-defined uncoupled states, particularly when

degenerate states are involved. This we feel is mostly due to the separation of space and spin, connected with an imbalance of symmetry constraints on the two parts. In our treatment we use spin-orbitals, which from the beginning puts space and spin on similar footing. A single configuration of spin-orbitals will, in general, not correspond to a proper spin-coupled state, but the atomic "valence states" remain rather well-defined, since each valence electron is accommodated in a distinct (apart from exchange) atomic orbital with a distinct spin.

One desires a configuration which allows one to describe the dissociation process as a smooth recoupling of the orbitals from a perfectly-paired state to the proper atomic states. Particularly attractive, in this regard, is the spin-valence theory employed by Heitler (1934), where eigenfunctions of the atomic Hamiltonians are coupled together to form the molecular state. In fact, this was the motivation behind McFitt's (1951) atom-in-molecule approach. The basic question is "how do we choose our spin-orbital occupations in our single-configuration, which has these desired properties, without falling into the traps that other methods do when all the proper couplings are not taken into account?" Before we answer this, let us mention two methods which come close in spirit to what we are about to describe. The first is Hund's rule coupling (Gerratt,

1971), and the second is alternate molecular orbital (AMO) theory (Fauncz, 1967). We mention them because of the physical picture they present; however, in these two related methods, space and spin are separated, and the resultant spin functions are complicated. We feel that if one instead uses spin-orbitals and relaxes some of the constraints<sup>1</sup> normally imposed on the spin (Gunnarsson *et al.*, 1977), then the same physical picture suggests a very simple scheme for making our assignments.

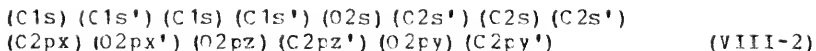
The procedure is to start out with a configuration which corresponds to a covalent structure that one generates from valence shell electron-pair repulsion theory (VSEPR) as described in any general chemistry text. The spins are assigned such that the electrons on each atom are coupled to give maximum resultant and such that the resultant spin on each atom alternates in sign with respect to each of its bonded neighbors. This should be done such that the total resultant spin is the desired one (if possible). Consider the example of a carbon monoxide molecule. It has the valid structure



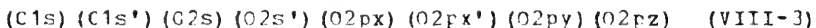
corresponding to the configuration

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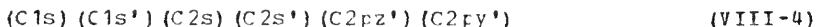
<sup>1</sup>These constraints were necessary in the other treatments to get proper separation of the atomic states. This is not necessary in our simple treatment.



where the primes denote opposite spin. There are of course ionic structures as well, but we shall incorporate them later. The main point here is that this structure separates into the atomic states represented by the configurations



and



each satisfying Hund's rule. This type of structure can be generated for any system where the atoms can be divided into two subsets in such a way that no two atoms which belong to the same subset are neighbors to each other. Such a system is called an "alternate" system. For nonalternate systems the situation can be quite different. In fact, in nonalternate solids this can give rise to antiferromagnetic conduction sheets.<sup>1</sup> In cyclic molecules (the only molecules which can be nonalternate) nonalternacy is often accompanied by unusually stable ions, radicals, "sandwich" complexes, or some higher level of alternacy.<sup>2</sup> Even though this would be an interesting topic on its own, we shall not dwell on it here. The main point we wished to make here is that within each atom we have parallel alignment of spins (Hund's rule,

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<sup>1</sup>For example, an FCC lattice might have alternating planes of parallel spin, thus a higher order of alternacy.

<sup>2</sup>Such as sigma and pi planes.

ferromagnetic coupling) and between atoms we have (at least for alternate systems) antiparallel alignment of spins (antiferromagnetic<sup>1</sup> coupling). This is, of course, just a general guideline, and one can make any occupation assignments one wants, provided that care is taken not to break symmetry with exchange polarization (the scheme just described will not break symmetry when applied to alternate systems).

So far we have just devised a way to assign spins such that we get smooth uncoupling upon separation. Suppose, though, that this single neutral structure does not properly describe the molecular state or the separated-atom states. What if we knew that the molecule had a triplet<sup>2</sup> ground state which can not be formed by a smooth<sup>3</sup> coupling of the separated-atom ground triplet<sup>2</sup> states? What if we suspect the ground state to be a great deal ionic in character? These types of questions involve what is perhaps best described as the crossing of different single-configuration diabatic states (O'Malley, 1971). The simplest procedure would be to compute both of the diabatic states involved and "uncross" them. In fact, for the first case where the curve

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<sup>1</sup>Not to exclude the possibility of complete ferromagnetic coupling.

<sup>2</sup>By "triplet" we mean two unpaired parallel spins; total spin is never properly taken into account in our treatment.

<sup>3</sup>"smooth" meaning no sudden charge transfer or spin flips.

crossing corresponds to a spin flip, this is about the only alternative one has in the present treatment; however, in the second case we only have charge transfer (no spin flips) taking place. This brings us to the main theme of this chapter - a self-consistent charge and configuration procedure.

As mentioned earlier there are other valid (ionic) structures one can write down for carbon monoxide besides the covalent one in (VIII-1). These other structures are nothing more than charge transfers from the covalent structure (dismissing spin flips). By employing fractional occupations in our configuration we can go smoothly from one structure to another (one diabatic state to another). In general, the molecular state itself might best be described by such a configuration with fractional occupations (configuration mixing) which goes "adiabatically" into the separated atomic states with integral occupations. How does one determine these fractional occupations? So far we have not even said what determines the molecular state in our treatment. One could just define it in terms of a given (valence-bond) structure constructed from the atomic orbitals, but most molecules probably can not be well-represented by a single structure. In chapter VI we developed a means of generating molecular (delocalized) orbitals from a model Hamiltonian built up from the atomic



orbitals and energies. Perhaps the best way to describe the molecular state then is in terms of these molecular orbitals. We could choose integral occupations for these molecular orbitals corresponding to some desired state and then let the population analysis determine the fractional occupations for the atomic orbitals which go into our single valence-bond structure. Such a procedure would be very much like the hyper-Hartree-Fock method proposed by Slater *et al.* (1969) for crystals. This type of procedure would allow one to compute a potential energy surface which by construction corresponds to a molecular state with a specific spin<sup>1</sup> and angular momentum<sup>1</sup>, as well as to a specified set of separated-atom states with the same net spin and angular momentum. Perhaps the best way to illustrate this is by an example, and the next chapter should serve this purpose.

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<sup>1</sup>Only the component along some chosen preferred axis is explicitly and uniquely specified.

CHAPTER IX  
APPLICATIONS

A. Nitric Oxide Molecule

Despite the important role of nitric oxide and its positive ion in the upper atmosphere and its ecologically undesirable presence in the exhaust emissions of our ever-so-popular automobiles down here on earth, there has been relatively little theoretical electronic structure work reported for this first-row diatomic molecule. Restricted Hartree-Fock and configuration interaction calculations have been carried out for the ground ( $X^2\Pi$ ) and first excited ( $A^2\Sigma^+$ ) states of nitric oxide at their equilibrium geometries by Green (1972, 1973) to yield one-electron properties with rather limited success.<sup>1</sup> But to our knowledge there has been no unrestricted Hartree-Fock calculation (spin-projected or otherwise) reported on this

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<sup>1</sup>See also the natural orbital calculation of Kouba and Chrn (1971).

odd-electron (paramagnetic), open-shell system to assess, on a one-electron basis, its complex photoelectron spectrum (Turner et al., 1970). Configuration interaction calculations for the positive ion have been done, however, in an attempt to assign the various observed states (11 between 9 and 24 eV) by Lefebvre-Brion and Moser (1966) and later by Thulstrup and Chrn (1972). The assignments appear to be resolved, although alternate assignments have been proposed by Collin and Natalis (1968).

We make no attempt here to confirm or challenge these assignments, but rather, to test our theory for its strengths and weaknesses on a reasonably small but complex system before applying it to a much more ambitious problem. Since our aim is to look into the chemisorption of nitric oxide on a nickel surface, perhaps we should know how the theory works on nitric oxide itself. From the outset we expect (or at least hope) that the dissociation process, in terms of the interaction of localized atomic orbitals and the associated total energy, should be reasonably well described, since the total energy is not dependent upon how the total density is broken up into various contributions but rather on the total density alone. On the other hand, properties associated with the delocalized molecular orbitals derived from our model Hamiltonian, such as Koopmans' energies, must be taken with less reliance. In

connection with this, charge transfer (between valence-bond structures, if you wish) is expected to be a sensitive issue. This too, in our procedure, depends on the model Hamiltonian used to generate the molecular orbitals from which the population analysis proceeds. For the most part, we will avoid such complications by restricting ourselves to single valence-bond-type structures, that is, no charge consistency will in general be attempted.

For nitric oxide in its ground ( $X^2\pi$ ) state, we will use the configuration

(C1s) (C1s') (N1s) (N1s') (C2s) (C2s') (N2s) (N2s')

(C2pz) (N2pz') (O2px) (N2px') (O2py) (N2py') (IX-1)  
in terms of "perfect-paired" atomic spin-orbitals where the primes denote the majority spin. This is unitarily equivalent to a molecular configuration

(1 $\sigma$ ) (1 $\sigma'$ ) (2 $\sigma$ ) (2 $\sigma'$ ) (3 $\sigma$ ) (3 $\sigma'$ ) (4 $\sigma$ ) (4 $\sigma'$ )

(5 $\sigma$ ) (5 $\sigma'$ ) (1 $\pi_x$ ) (1 $\pi_x'$ ) (1 $\pi_y$ ) (1 $\pi_y'$ ) (2 $\pi_y'$ ) (IX-2)

where the 2 $\sigma$ , 4 $\sigma$  and 2 $\pi_y$  orbitals would be of antibonding character and the 1 $\sigma$  and 1 $\pi_y$  orbitals of rather nonbonding character. In our procedure, the nitrogen and oxygen orbitals in (IX-1) are determined separately in an alternating fashion coupled to each other in a self-consistent manner as described in earlier chapters. From these atomic orbitals, a model Hamiltonian is constructed whose natural orbitals (canonical Hartree-Fock solutions) correspond roughly to the molecular orbitals in (IX-2).

The basis sets used for nitrogen and oxygen are STO's of double-zeta quality (Roetti and Clementi, 1974) plus d-type polarization functions, for a total of 15 functions on each atom. The model potentials were expanded in a set of 4 s-type functions and one p-type function polarized along the bond axis (z-direction here). We chose an even-tempered set of exponents (0.5, 1.0, 2.0, 4.0) scaled by the cube root of the nuclear charge, as suggested in chapter IV. The exponents for the basis sets and the model potentials are listed in Tables 1 and 2. No attempt was made to optimize these exponents, and the polarization functions were selected rather arbitrarily.

The first calculation was carried out at the equilibrium geometry of 2.17 a.u. with the procedure just described above and in previous chapters, but the spin-orbital occupation numbers were kept fixed. In other words, any charge transfer predicted from the population analysis between each cycle was ignored. As stated above, this corresponds to a single valence-bond-type structure. This is done to eliminate any effects due directly or indirectly to the model Hamiltonian. The result was a total energy of -129.44 a.u., which is about 0.10 a.u. below the estimated Hartree-Fock limit (Hollister and Sinanoglu, 1966). The subsequent model (FWMC) Hamiltonian calculation, however, gave molecular orbital energies which were essentially in

Table 1. Basis sets for nitrogen and oxygen.

Type	nitrogen <sup>a</sup>	oxygen <sup>a</sup>
1s	8.49597	9.46635
1s	5.98644	6.83768
2s	2.26086	2.68801
2s	1.42457	1.67543
2p	3.24933	3.69445
2p	1.49924	1.65864
3d	2.00000 <sup>b</sup>	2.00000 <sup>b</sup>

<sup>a</sup> From the tables of Roetti and Clementi (1974).

<sup>b</sup> Unoptimized polarization function.

Table 2. Model potential exponents for nitrogen and oxygen.

Type	nitrogen <sup>a</sup>	oxygen <sup>a</sup>
1s	0.95647	1.00000
1s	1.91293	2.00000
1s	3.82586	4.00000
1s	7.65173	8.00000
2pz	1.91293 <sup>t</sup>	2.00000 <sup>b</sup>

<sup>a</sup> Even-tempered set of functions (0.5, 1.0, 2.0, 4.0) scaled by  $Z^{**}(1/3)$ .

<sup>t</sup> Polarization function along bonding axis (1.0).

reverse of the observed order for the  $5\sigma$  and  $2\pi_y$  orbitals, and gave an anomalous  $3\sigma$  orbital 50 eV below the observed value.

In an effort to see what the source of these discrepancies was (assuming that Koopmans' approximation is not all to blame), a second calculation was performed where charge transfer was allowed to take place, that is, charge-consistency was attained. The result was a somewhat higher total energy, with some improvement in the molecular orbital energies, but the basic discrepancies persisted. The net charge transfer was only 0.015 (from oxygen to nitrogen!), which suggests that the single (neutral) valence-bond structure is perhaps not so inadequate. Could it be that the model Hamiltonian constructed from just the occupied<sup>1</sup> atomic orbitals is too poor?

The next logical step appeared to be an improvement of the model Hamiltonian. As mentioned in chapter VII, the inclusion of virtual<sup>1</sup> orbitals in the EOMO Hamiltonian required either complex arithmetic (a drastic and undesirable step) or an alternate method of treating the nonorthogonality which subsequently alters the population

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<sup>1</sup>With respect to the model Hamiltonian, "occupied" merely implies a negative orbital energy and "virtual" a positive energy.

analysis. The second alternative requires an extra diagonalization of the metric matrix (if Löwdin's (1970) symmetric orthogonalization is used) but is much easier to implement computationally. This leads to a population analysis which is, in part, arbitrary if done in the orthogonal basis (which is necessary to guarantee reasonable occupation numbers in a charge-consistent calculation). Such a calculation was performed. There was a substantial improvement but the relative ordering of the orbital energies was still in disagreement with the observed values as they have been assigned. Charge consistency gave little more improvement. The main discrepancies are in the relative order of the various singlets<sup>1</sup> and triplets<sup>1</sup> and the apparent reversal of the 5<sub>g</sub> and 2<sub>g</sub> levels.

One final improvement, still involving the virtual orbitals, was attempted. In the model Hamiltonian, as constructed above, the virtual orbitals play a role equivalent to that of the occupied, and the energy associated with each virtual orbital should then be the energy it would have if it were indeed occupied. This is related to the problem encountered in configuration interaction and many-body-perturbation calculations, where

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<sup>1</sup>The terms "singlet" and "triplet" refer to the final ionic states resulting in the deletion of a majority- or minority-spin orbital, respectively (the "singlet" actually being an average of singlet and triplet states).



the Hartree-Fock virtual orbitals used in their expansions arise from a potential generated by too many electrons. This erroneous potential comes about from a miscancellation of Coulomb and exchange interactions an electron has with itself. This cancellation is an important artifact, however, of the Hartree-Fock method which allows the use of a single operator for all the occupied (and virtual) orbitals (Huzinaga, *et al.*, 1973). An approximate first-order correction to this can be achieved by just rescaling the Coulomb and exchange contributions to the orbital energies to account for the proper number of particles involved in the potential. For a charge-consistent calculation this involves all partially occupied orbitals, each with its own scaling factor. Such a correction was made and the results are given in Table 3, along with the experimentally observed values and other calculated results. In Figure 2, a simulated photoelectron spectrum is shown where the profiles are generated by gaussians of constant half-width (FWHM=0.5eV) weighted by the spin-degeneracy of the resultant ionic states. The inset is a tracing of the ESCA result (Siegbahn *et al.*, 1969). The prevailing feature is a shift to higher energies, particularly for some of the triplet states relative to the singlets. In order to retain a total energy which is independent of the model Hamiltonian, the occupations again were kept fixed in this calculation. The atomic orbitals, also independent of the

Table 3. Calculated and experimental ionization potentials for nitric oxide ( $X^2\pi$ ).

Ion state	a MO	b expt	c expt	d expt <sup>†</sup>	this calc	e calc	f calc
$1\pi$	$O1s'$	544.0			564.2		
$3\pi$	$O1s$	543.3			565.4		
$1\pi$	$N1s'$	411.8			425.1		
$3\pi$	$N1s$	410.3			422.1		
$1\pi$	$3\sigma'$	43.8			51.2		
$3\pi$	$3\sigma$	40.6			47.6		
$1\pi$	$4\sigma'$	23.3			28.0		21.0
$3\pi$	$4\sigma$	21.7			29.9		20.0
$A1\pi$	$5\sigma'$	18.5	18.3	18.3	18.6	19.4	17.8
$3\pi$	$5\sigma$	16.7	16.5	17.2	16.1	17.0	16.9
$1\Sigma^+$	$1\pi y'$				17.8		18.3
$1\Delta$	$1\pi x'$		19.3	18.9	15.8	17.7	17.8
$1\Sigma^-$			18.4	17.3		17.0	17.2
$3\Sigma^-$			17.6	16.6		17.0	17.0
$3\Delta$	$1\pi x$		16.8	15.7	21.9	16.0	16.1
$a^3\Sigma^+$	$1\pi y$	14	15.7	14.0	19.4	15.0	14.3
$x^1\Sigma^+$	$2\pi y$	10	9.3	9.3	15.8	9.3	12.0

a

Via Koopmans' theorem.

b

ESCA, Siegbahn *et al.* (1969). (Vertical)

c

Turner *et al.* (1970). (Adiabatic)

d

Collins and Natalis (1968). (Adiabatic)

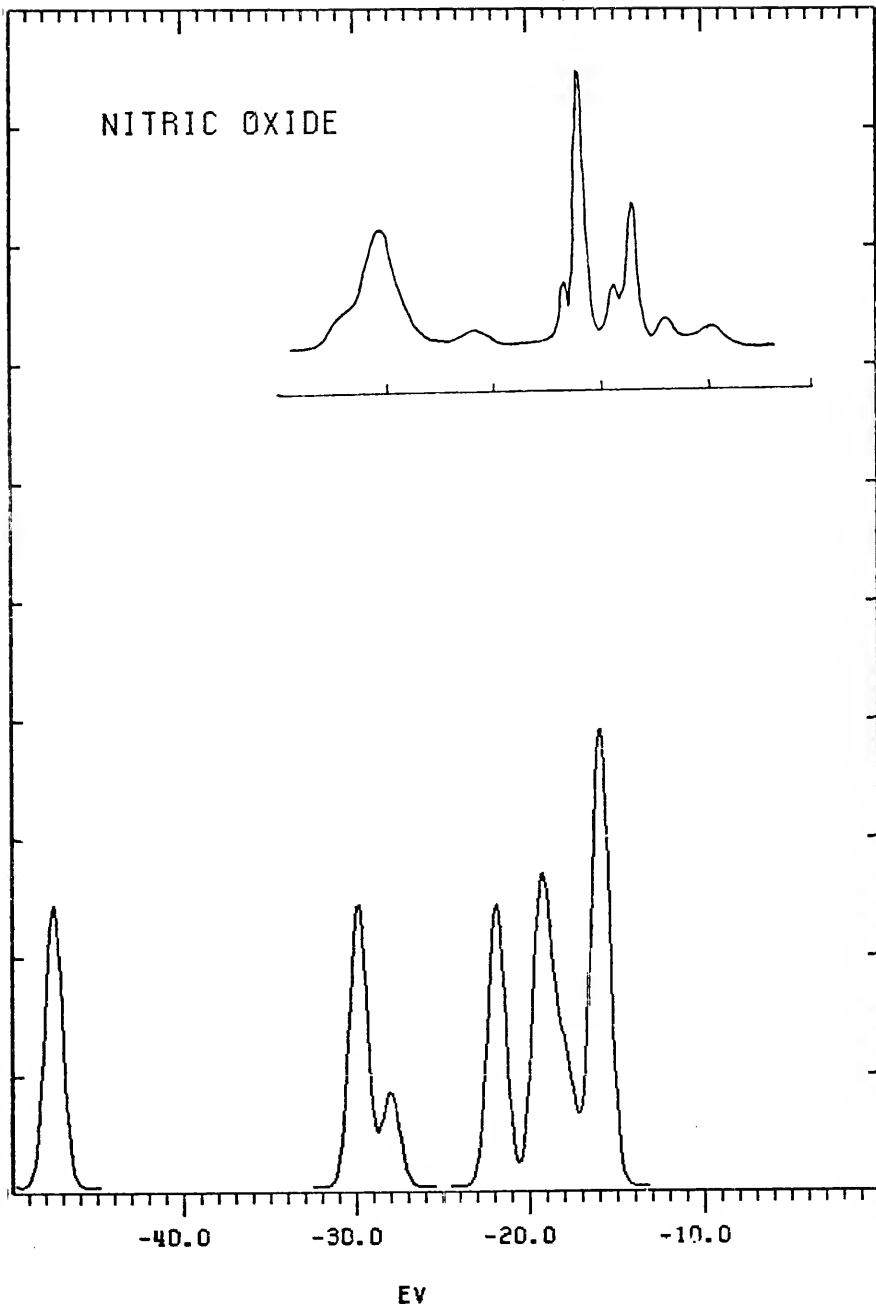
e

Lefebvre-Brion and Moser (1966). (Adiabatic)

f

Thulstrup and Ørtn (1972). (Adiabatic)

Figure 2. Calculated and experimental photoelectron spectra for nitric oxide ( $X^2\Pi$ ). Convolution done with gaussians with FWHM=0.5eV. Inset from ESCA (Siegbahn, et al., 1969).



model Hamiltonian, are illustrated in Figures 3 and 4 by "hidden-line" plots (McIntosh, 1975) in the yz-plane for nitrogen and oxygen respectively. The inclusion of virtual orbitals in the model Hamiltonian tends to be a sensitive issue as can be the charge transfer, but unlike the charge transfer problem, it has no direct effect on the total energy or the atomic orbitals, provided the occupations are restricted to zero and unity.

At this point, one might begin to have some doubts about the various approximations used in our treatment, or the use of a single nonsymmetric spin-polarized valence-bond configuration. One must reserve judgement, however, until each of these approximations has been carefully examined on a variety of systems, for one can not help but single out the model Hamiltonian as still a prime target of scrutiny. One might also be suspect of Koopmans' approximation for this system. A spin-projected unrestricted Hartree-Fock<sup>2</sup> calculation would help in this regard.

Let us now look at what should be a more promising side of this story. The total energy that we obtained at the equilibrium geometry (with fixed occupations) was about 6 eV

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<sup>2</sup>A spin-polarized X-alpha calculation of Connolly *et al.* (1973) is in reasonable agreement with experiment.

<sup>1</sup>Using the same basis and Grand-Canonical Hartree-Fock.

Figure 3. "Hidden-line" plots of the atomic orbitals on the nitrogen atom. yz-plane ( $x=0.0$ ).

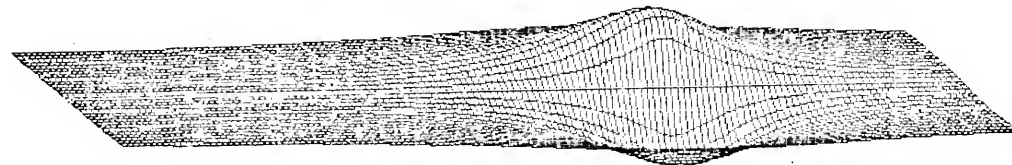
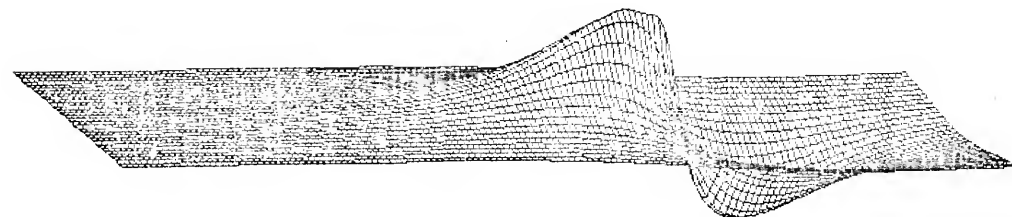
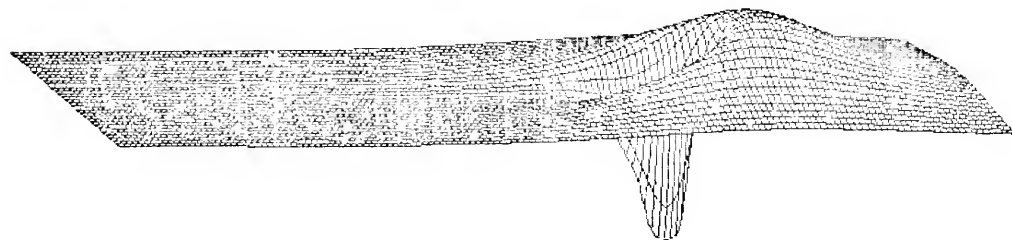
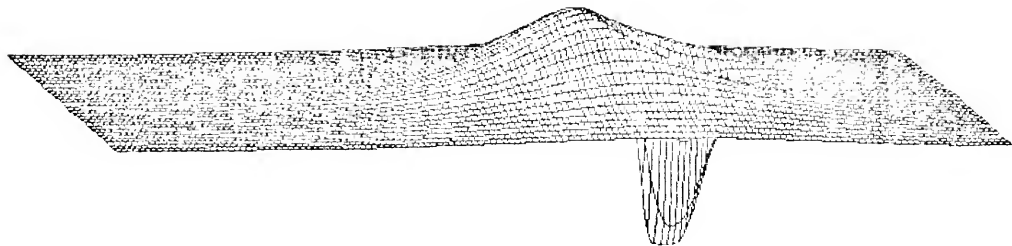
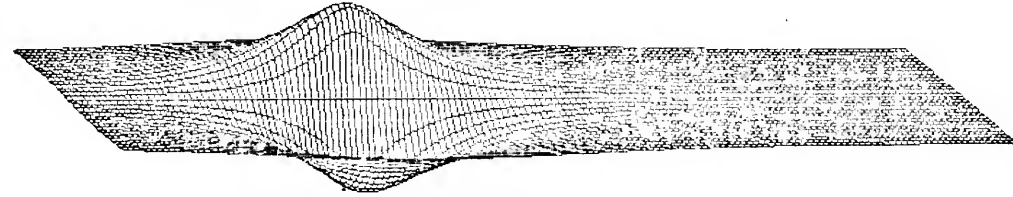
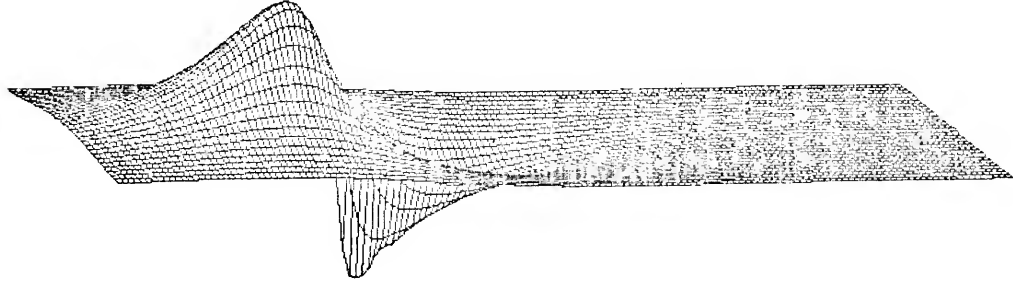
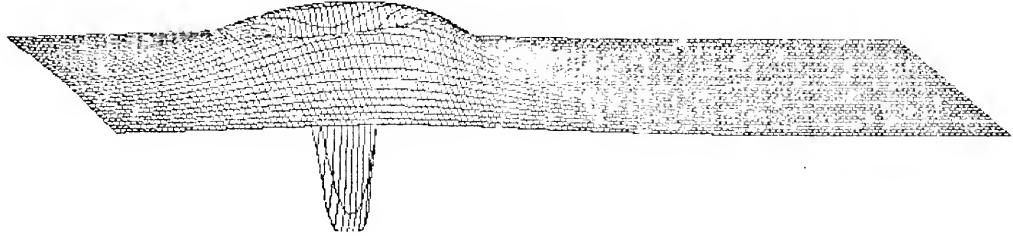
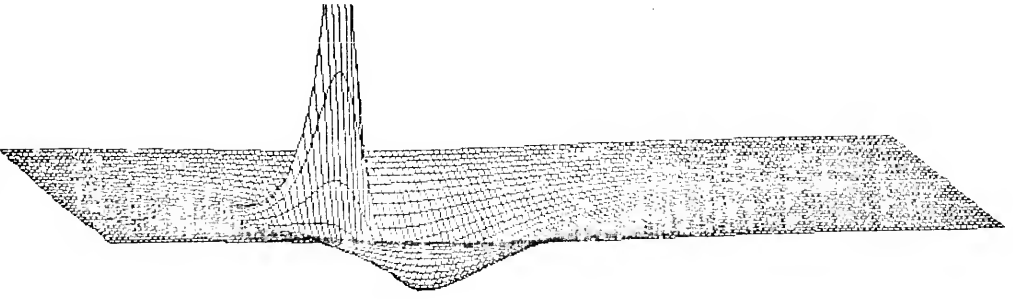


Figure 4. "Hidden-line" plots of the atomic orbitals on the oxygen atom. yz-plane ( $x=0.0$ ).





lower than that of the separated Hartree-Fock atoms.<sup>1</sup> The experimental dissociation energy is 6.5 eV. This is either fortuitous or very encouraging. A full potential energy curve is certainly in order at this point. For the most rapidly convergent procedure, one starts the potential energy curve at the separated-atom limit where one is guaranteed the proper limit (by construction) and proceeds along the curve toward smaller interatomic distances, using the results of each calculation as a starting point for the next. This procedure is particularly important for charge-consistent calculations (which is not the case here, however). The results of these calculations are presented in Figure 5 and summarized in Table 4. The spectroscopic constants are determined by a least-squares fit to the Hulbert-Firschfelder (1941) modified Morse potential function and interpolation is generated by a cubic spline.<sup>1</sup> The agreement with experiment is quite remarkable - so much, in fact, that one is a little reluctant to stake any claims as to its veritability.

It appears that we have witnessed both extremes of our earlier expectations. Perhaps, though, the latter success for the potential energy curve for  $\text{NO}(X^2\Pi)$  can offer recourse to a resolution of the apparent failure to describe

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<sup>1</sup>Program written by Nelson H. F. Beebe, (Quantum Theory Project, University of Florida, Gainesville, Florida).

Figure 5. Calculated and experimental (Morse) potential energy curves for  $\text{NO}(X^2\Pi)$ .

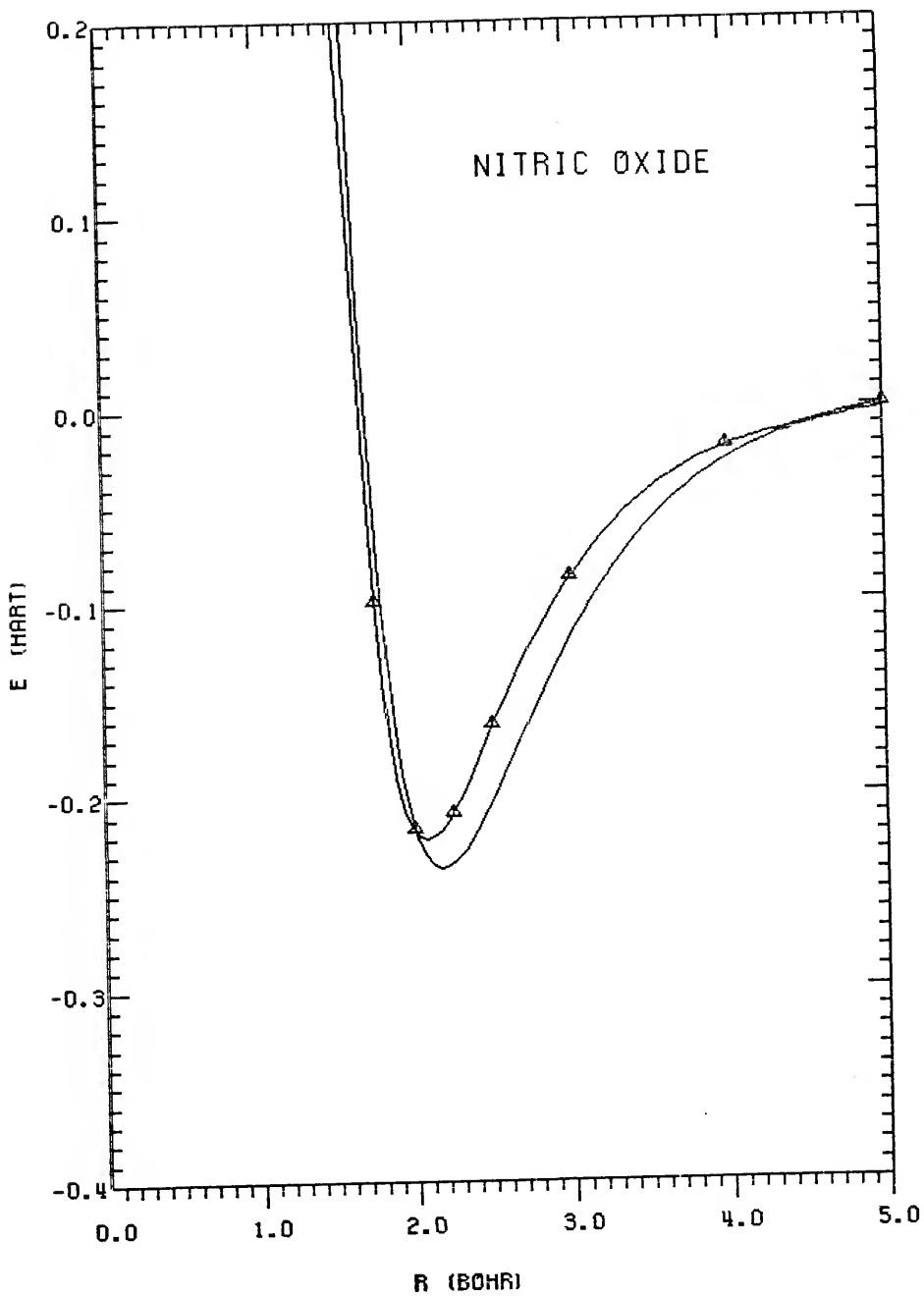


Table 4. Calculated and experimental spectroscopic constants for nitric oxide ( $X^2\Pi$ ).

Constant	a expt	this calc	t calc
$r_e$ ( $\text{Å}$ )	1.15	1.10	1.25
$w_e^{-1}$ ( $\text{cm}^{-1}$ )	1904	1993	1731
$w_x e e^{-1}$ ( $\text{cm}^{-1}$ )	14	20	24
$B_e^{-1}$ ( $\text{cm}^{-1}$ )	1.70	1.86	1.45
$\alpha_e^{-1}$ ( $\text{cm}^{-1}$ )	0.018	0.032	0.023
$D_e$ (eV)	6.5	6.0	3.8

a Herzberg (1950).

b Thulstrup and Øhrn (1972), uses same spline fit as in present work.

the ionization process. That is, one might anticipate similar success in computing the potential energy curves for the various states of  $\text{NO}^+$  for a direct calculation of the ionization potentials. We shall end the treatment of nitric oxide on this hopeful note since our real aim here is somewhat different.

### B. Nickel(100) Surface

Much has been said in these energy-conscious times about the importance of the study of surfaces and of chemisorption on them in the field of catalysis, and the recent growth of interest in this field has spawned significant advances in both theory and experiment. Ultrahigh vacuum techniques coupled with an endless variety of optical, electron and other spectroscopic measurements provide the surface scientist with the tools to help understand the nature of surfaces and the electronic structure of surface-adsorbate complexes.<sup>1</sup> On the theoretical side, various approaches stem from both solid-state band theory and theories generally applied to molecular complexes; however, we are still far from possessing a reliable computational method for a

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<sup>1</sup>See, e.g., *Physics Today*, 28(4), April 1975; issue devoted to surface physics.

satisfactory description of the chemisorption bond.<sup>1</sup> One needs a method as simple as extended Hückel theory (Wolfsberg and Helmholtz, 1952; Anderson and Hoffmann, 1974) which is self-consistent and contains no empirical parameters.

The approach we take here is, of course, a localized one with respect to the role of the surface in the chemisorption bond. In order to avoid the effects of cluster boundaries, we shall compose a finite atom-cluster model built up from atoms which retain their "bulk", "surface" and "adsorbate" identities. Each atom in the cluster will still "feel" the influence of at least its nearest-neighbor environment, even though these neighbors may not be explicitly in the cluster. This, we feel, is a very important feature to be incorporated in small-cluster simulations of extended systems. One would like to have a "surface" cluster which does not have surface of its own, so to speak. We shall construct our model in three steps.

The first step is to characterize the bulk, and by this we mean a self-consistent description of an atom in the metal. In the case of nickel, we have a face-centered-cubic (FCC) lattice which from the viewpoint of a single atom is a

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<sup>1</sup>See Bullett and Cohen (1977a) and references therein for a short synopsis of current techniques.

nearest-neighbor shell of 12 other atoms in a cuboctahedral arrangement (see top structure in Figure 6), each of which sees the same environment about it, and so on, to complete the fully extended bulk arrangement. As a first approximation, we will consider nearest-neighbor interactions only. The self-consistent calculation proceeds as follows. We start with a free atom calculation<sup>1</sup> using the hybrid single-double-zeta basis given in Table 5 and a spherical 4-term model potential expression with the exponents in Table 6. We then take 13 of these atoms with their free-atom orbitals, energies and model potentials, and arrange them as in Figure 6 (top).<sup>2</sup> The experimental lattice constant of 4.7 a.u. is assumed throughout. The next calculation is on the central atom in this cluster with the 12-free-atom environment taken fully into account. Now comes the first important step toward self-consistency. We take the results of the central atom and place them at the 12 neighbor sites and repeat the central atom calculation with this modified environment. This process is repeated until the central atom and its neighbors "coincide". The eigenvalue spectrum of this self-consistent "atom-in-metal" is shown in Figure 7, compared to that of the free atom. One could, in principle, extend this into a band calculation

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<sup>1</sup>An unrestricted Grand-Canonical Hartree-Fock calculation for the  $3F$  state ( $d^8$  configuration).

<sup>2</sup>Ferromagnetic coupling (triplet pairing) of spins.



Figure 6. Cluster models for the bulk, surface and four-fold hole adsorption site.

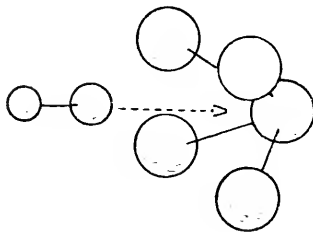
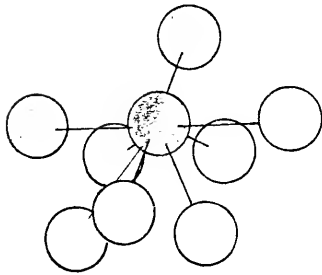
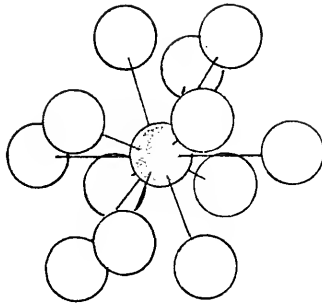


Table 5. Basis set for nickel.

Type	exponent <sup>a</sup>
1s	27.3470
2s	10.1098
2p	12.0478
3s	4.9860
3p	4.6940
3d	6.7055
3d	2.8738
4s	2.0771
4s	1.1389

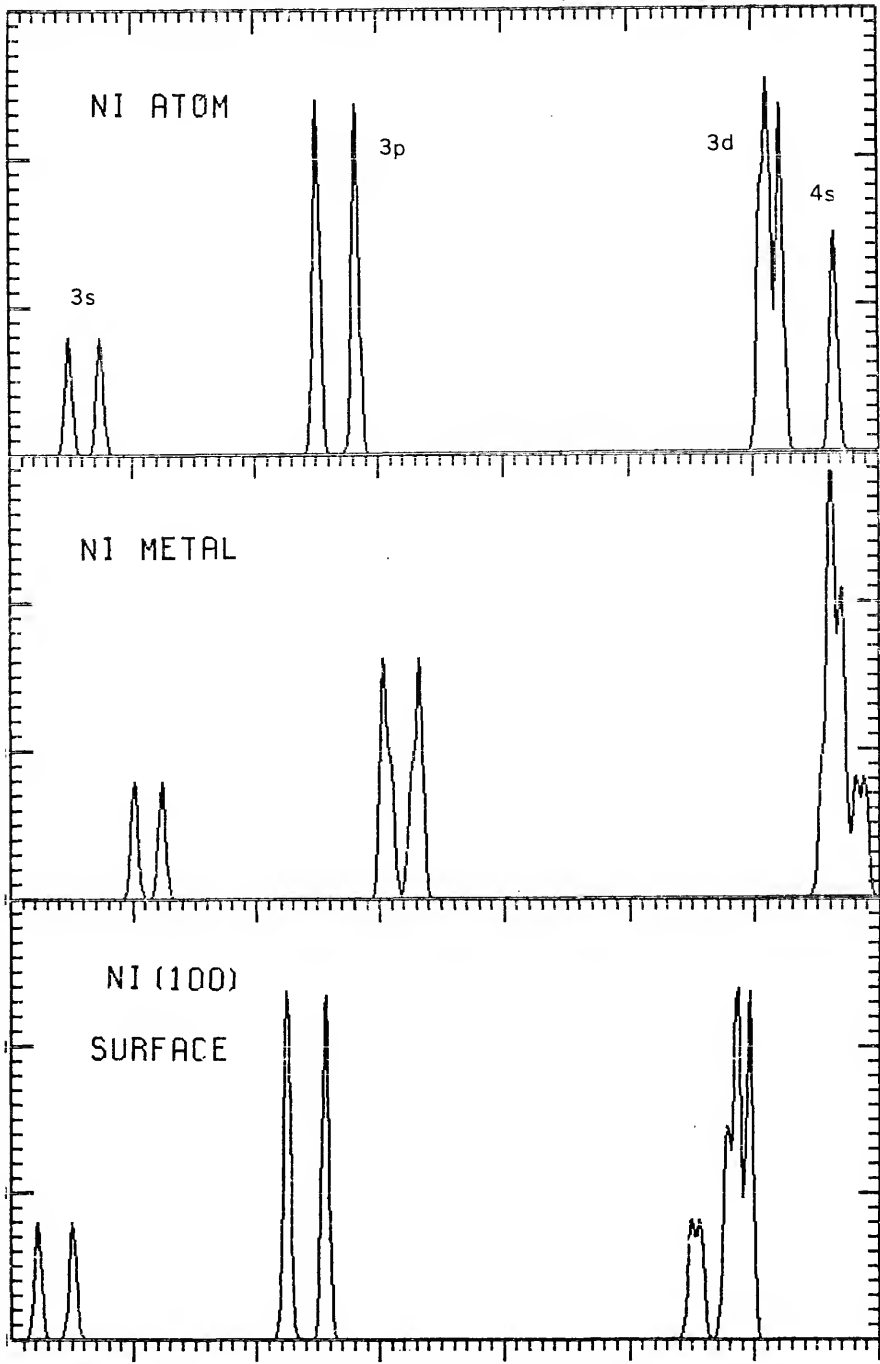
<sup>a</sup> Mixed single- and double-zeta basis of Roetti and Clementi (1974).

Table 6. Model potential exponents for nickel.

Type	exponent <sup>a</sup>
1s	1.5193
1s	3.0366
1s	6.0732
1s	12.1464

<sup>a</sup> Even-tempered set (0.5, 1.0, 2.0, 4.0) scaled by  $Z^{**}(1/3)$ .

Figure 7. Calculated photoelectron spectra of Ni(atom), Ni(metal), and Ni(surface). (range 0-140eV).



just as with the renormalized-atom approach (Hodges et al., 1972) and in a certainly more elegant, if not superior, fashion. Such a venture has not been undertaken to date, however.

The next step is to characterize the nickel(100) surface. Analogous to a bulk atom, a (100)-surface atom has only 8 nearest neighbors (see middle structure in Figure 6), if we ignore any distortions for the moment. As a first approximation, we can consider the top layer as being the only layer which is different from those in the bulk. We shall also, as in the bulk case, consider only nearest-neighbor interactions. From transform-deconvoluted LEED (low energy electron diffractor) experiments (Lardman and Adams, 1974) the (100)-surface layer spacing is within 1% of the bulk value for Ni(FCC), so no distortions in the geometry need to be taken into account. Now, since four of the atoms in our model cluster are in a "bulk" layer, we hold them fixed in their "bulk" state (same orbitals, energies, model potentials, etc.). The other four are surface atoms identical to the central atom. We will thus proceed as before with a calculation for the central atom taking into account its full nearest-neighbor environment (the other four surface atoms starting out in their bulk states), and then iterate, by replacing the four neighboring surface atoms with the results of the central atom

calculation, until self-consistency is reached. For practical reasons yet to be worked out, the calculation for the nickel surface did not converge. Despite various damping techniques employed, only four iterations could be obtained before strange things happened. The eigenvalue spectrum for the fourth iteration is displayed in Figure 7 along with that of the free atom and the metal atom results. It was also necessary to hold the model potential fixed to its free atom value, and for consistency, the bulk calculation was redone using the same model potential (the differences were minor, however). The shift to higher binding energies is somewhat unexpected and is perhaps only an artifact of the convergence anomaly, but we shall take what we can get and proceed.

The last step is the construction of a model cluster representing the most likely site for adsorption. Based on theoretical and experimental studies of H, O, and CO on Ni(100) surface (Bullett, 1977b), the preferred site for adsorption is most likely a four-fold hole site. This was also the site chosen for a previous calculation of nitric oxide on nickel by Batra and Brundle (1976). Nearest-neighbor interactions for this site would involve 5 nickel atoms - four "surface" atoms and one "bulk" atom (see bottom structure in Figure 6). We are now ready to bring the adsorbate into the picture.

### C. Nitric Oxide on Nickel(100) Surface

The catalytic reduction of nitric oxide (by hydrogen) over noble metal surfaces is a reasonably well-known process (Kobylinski and Taylor, 1974). It is, in fact, the underlying process of the catalytic converters installed in newer emission-controlled automobiles (did you ever wonder where that "ammonia smell" came from?). We are not quite ready to tackle the actual chemistry that takes place on such a surface, but we can try to entertain a couple of questions that some recent experiments have left unanswered. Nickel is not a noble metal, but it is a known catalytic agent for many reactions involving the dissociation of a nitrogen-oxygen bond, such as the reduction (by hydrogen) of nitric compounds to amines (Morrisson and Boyd, 1966) which is probably the most important synthetic route in aromatic chemistry (the introduction of other groups into aromatic



rings via a diazonium group which is readily obtained from primary amines), since nitro compounds are easily prepared by direct nitration.

So why do we want to look at nitric oxide on a nickel(100) surface? One might think of this as a prototype system for the type of reactions just mentioned, but more specifically, recent X-ray (XPS) and ultraviolet (UES) studies of nitric oxide and nitrogen dioxide interactions with nickel (Brundle, 1976), and infrared (IR) data for nitric oxide on nickel (Blyholder and Allen, 1965) have posed a couple of interesting questions. There is reasonable evidence to suggest that nitrogen dioxide dissociates on nickel even at very low temperatures (80°K) leaving nitric oxide and atomic oxygen adsorbed on the surface. There is not enough data, though, to say that the direct reaction of nitric oxide with nickel produces the same species on the surface (same adsorption site, same orientation, same electronic state, etc.). Upon warming (to 300°K), adsorbed nitric oxide slowly dissociates into nitride- and oxide-like species; however, the former reaction is accompanied by the loss of atomic nitrogen. Subsequent reaction at this temperature with nitrogen dioxide and nitric oxide, respectively, produce very similar XPS and UES spectra, with loss of nitrogen, and, in the latter case, the appearance of a new weakly bound state of

nitric oxide (easily described on heating in vacuum). The UPS spectra under these conditions were uninterpretable. There is good reason to believe that nitric oxide is most strongly bound with nitrogen oriented toward the surface in a four-fold hole site perpendicular to the surface plane. However, could it be that nitrogen dioxide initially condenses with oxygen oriented toward the surface (since both ends have exposed oxygen atoms) and then dissociates to leave oxygen bonded nitric oxide on the surface which later dissociates (upon heating) to give off nitrogen? Could the weakly adsorbed state observed during extensive reaction with nitric oxide also be a reversed orientation of nitric oxide which then also dissociates to yield nitrogen? In the IR spectrum of nitric oxide on nickel a weak unassigned band occurs which has been attributed to a different adsorption site. But perhaps this too can be accounted for by this alternate orientation. Thus, if one could calculate the binding energies for nitric oxide on nickel in both orientations and predict the observed shifts in the UPS and XPS spectra, it would certainly lend support to this hypothesis. A more ambitious check would be to compute a potential energy curve for the nitrogen-oxygen stretch in this alternate orientation and predict the observed unassigned frequency in the IR spectrum.

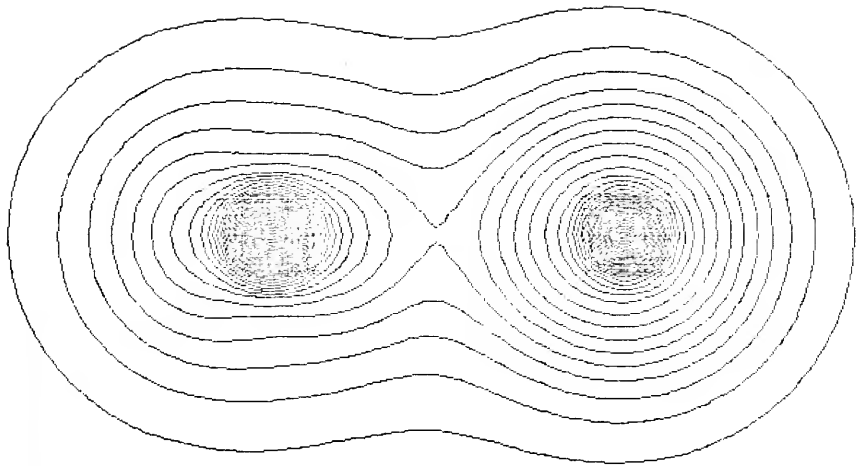
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\*New with respect to the original UPS and XPS spectra of directly adsorbed nitric oxide before further reaction was allowed to take place.

Our first calculation was on a cluster of 5 nickel atoms arranged as in Figure 7 (bottom) with the nitrogen atom oriented toward the surface and the spins antiferromagnetically aligned with the ferromagnetic surface (one might think of the entire surface cluster as a single Hund's-rule atom). The nickel lattice constant was left unaltered at 4.7 a.u., the nitrogen-nickel distance was set at 3.7 a.u.<sup>1</sup> (for all four surface atoms), and the nitrogen-oxygen distance was kept at its equilibrium molecular distance of 2.17 a.u. As mentioned in the previous section, the orbitals and model potentials for the nickel atoms were fixed at the bulk and surface values; however, the corresponding energies were computed correctly for their environment. This is only a first approximation but the next level of approximation would require (without reprogramming at this point) a much larger cluster in order to include a proper environment for the surface nickel atoms (with proper stoichiometry). For a coordinate-1 site (on top of a nickel atom) this could have been done with the nine-atom cluster in Figure 7 (middle). The total density for nitric oxide (contributions from nitrogen and oxygen atomic orbitals) is shown in Figure 8 (bottom) compared to molecular nitric oxide (top). The plot plane in this figure is 0.3 a.u. above the yz-plane to suppress the 1s

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<sup>1</sup>Taken from nickel oxide lattice.

Figure 8. Total density contours for nitric oxide (top) and nitric oxide on nickel(100) surface (bottom). ( $x=0.3$  a.u.)



O

N

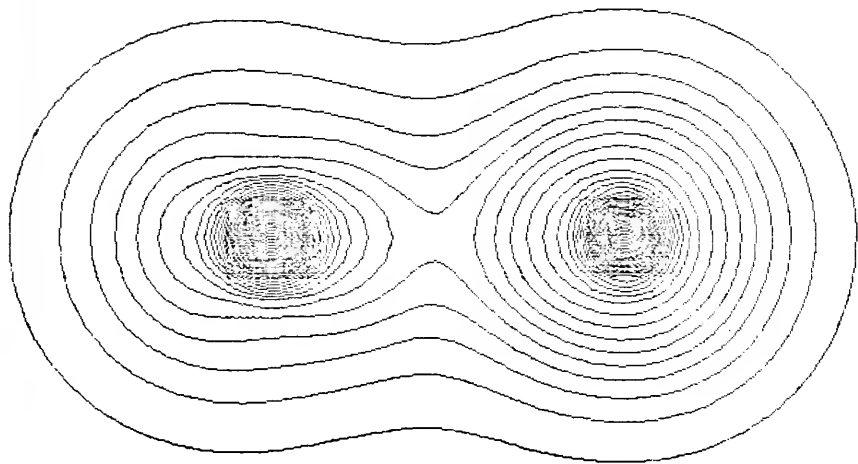
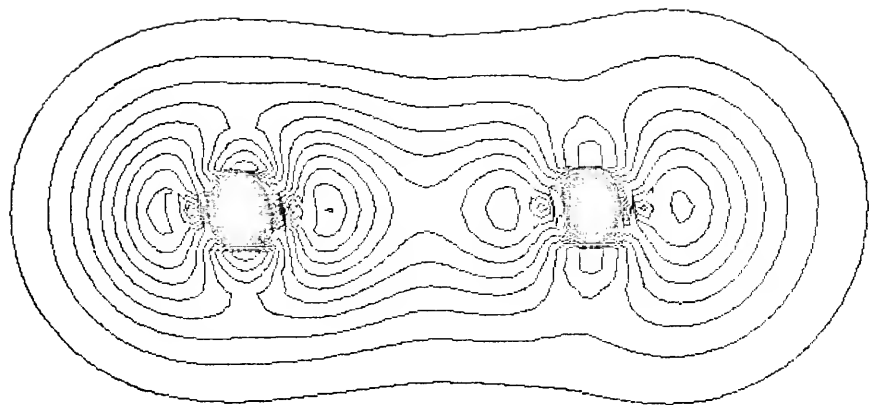


Figure 9. Sigma density contours for nitric oxide (top) and nitric oxide on nickel(100) surface (bottom).



O

N

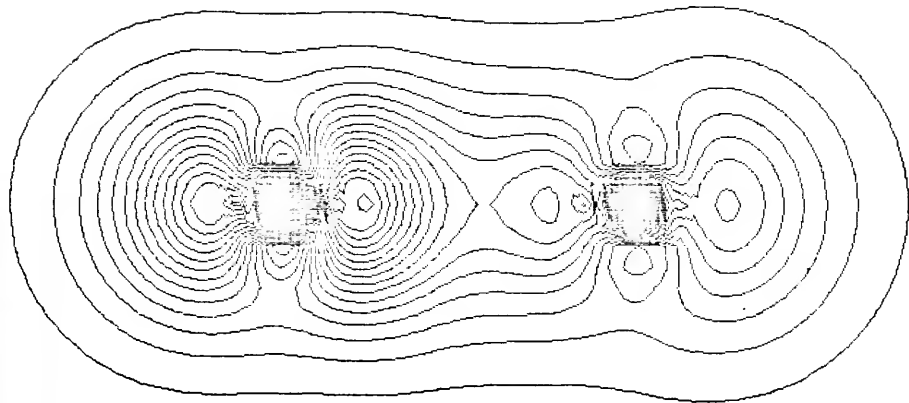
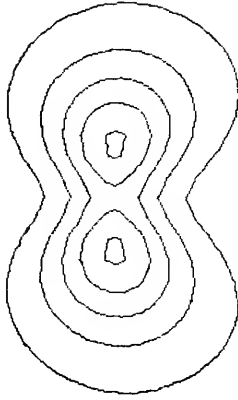


Figure 10.  $E_i$  density contours for nitric oxide (top) and nitric oxide on nickel(100) surface (bottom).

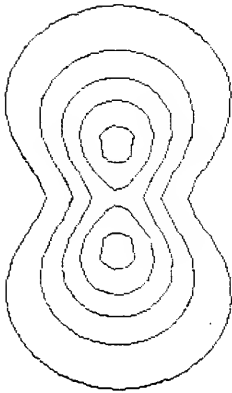




O



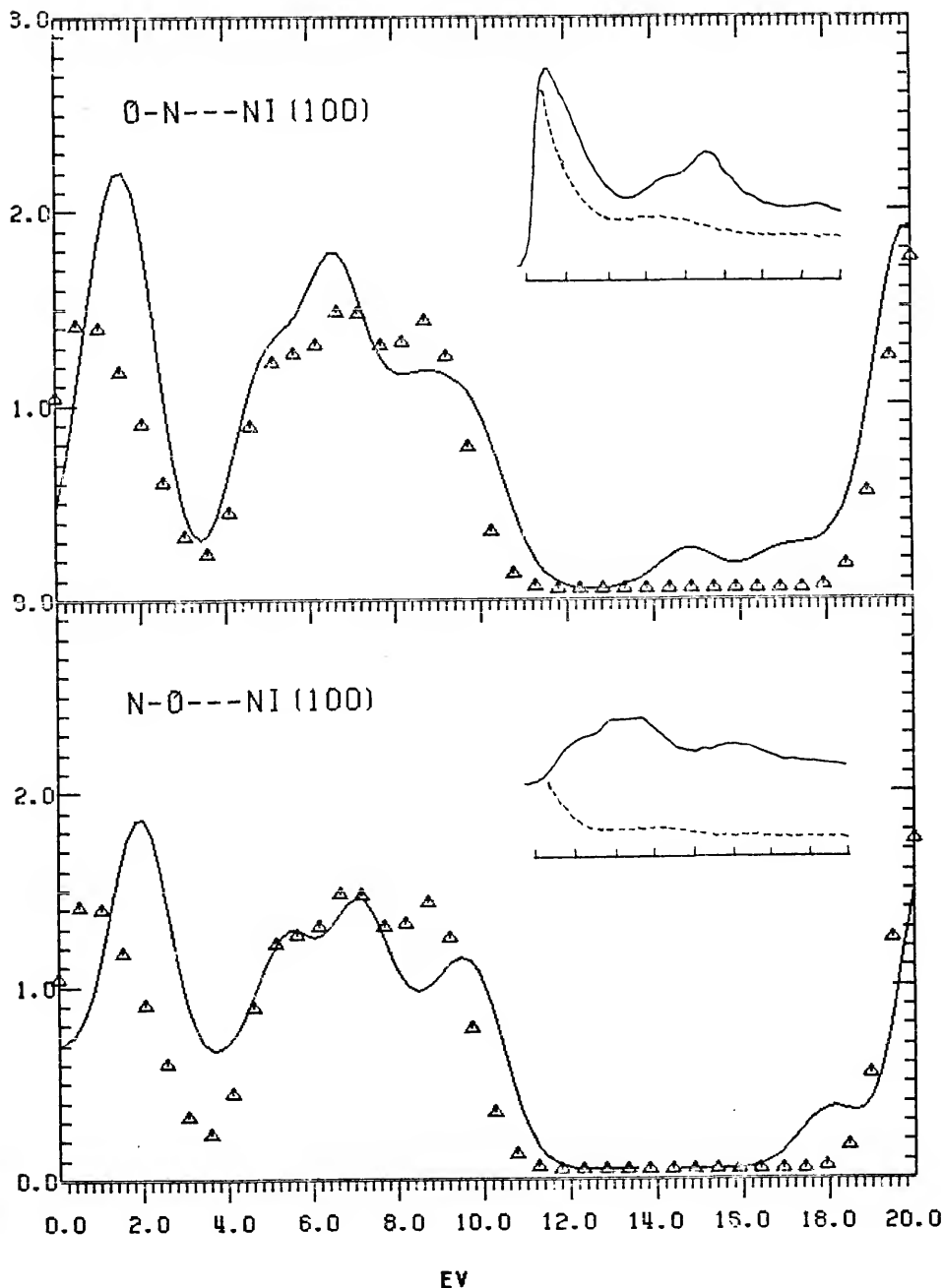
N



contributions at the nuclei. The contours in these plots are not necessarily at the same values so the comparison here is not too revealing of any dissociative character in the bond. In Figures 9 and 10, we show the valence sigma and pi contributions separately (in the yz-plane this time) to demonstrate more clearly the tendency toward nonbonding character. The total energy was about 1 eV lower than that of the separated nitric oxide molecule and clean surface (cluster), which is rather small for a molecule which is supposedly strongly adsorbed to the surface. The model Hamiltonian calculation (with virtual orbitals excluded for subtle computational reasons) gave valence electron binding energies (Koopmans' approximation, of course) which are displayed in Figure 11. The gaussian half-width was 0.7 eV and the triangles represent a calculation on the surface cluster alone. The inset is a tracing of the UPS spectrum for nitric oxide on nickel (at 80°K).

The second calculation was identical to the first except nitrogen and oxygen were interchanged and the spins were coupled in an analogous fashion as before. The corresponding results are also shown in Figure 11. Here the inset is a tracing of the UPS spectra for adsorbed nitrogen dioxide after extensive reaction at elevated temperature (300°K) which is reported to be very similar to that of just adsorbed nitric oxide under the same conditions. It is

Figure 11. Calculated valence binding energies for nitric oxide on nickel(100) surface. (FWHM = 0.7 eV). Triangles denote surface-only calculation. Insets are experimental UPS spectra of Brundle (1976).



under these conditions where the alternate orientation is suspected of contributing most to the spectrum. The general shift toward higher binding energies is evident in both the calculated and experimental results. The similarity of the calculated and experimental spectra is a little misleading unless one carefully subtracts the surface contributions in each case and recall that the experimental "zero" is at the Fermi level. Furthermore, an attempt to assign the nitric oxide peaks was in disagreement with that of Batra and Brundle (1976), as one might expect, from the discussion in the first section of this chapter. The XPS spectra is much more definitive. There is an obvious appearance of a different species in these spectra for nitric oxide and nitrogen dioxide under these same conditions. The nitrogen and oxygen 1s core binding energies were computed using the transition state method where half an electron is removed from the "ionized" orbital. The results are presented in Table 7. The general shifts are again accounted for by these two orientations.

As a final check on our supposition, a potential energy curve for the oxygen bonded orientation of nitric oxide was performed. The oxygen was kept at its original distance from the surface (3.7 a.u. from each surface atom) while the nitrogen-oxygen distance was varied perpendicular to the surface. The results are represented by the curve (\*) in

Table 7. Calculated and experimental core(1s) binding energies for nitric oxide on nickel(100) surface.

(eV)	N1s	O1s
Ni-N-C		
Calc	415.5	544.0
Expt <sup>a</sup>	400	531
Ni-C-N		
Calc	417.4	548.9
Expt <sup>t</sup>	403	532

<sup>a</sup> Brundle (1976).

<sup>t</sup> Attributed to different state of nitric oxide.

Figure 12 compared to the calculated curve for nitric oxide ( $\Delta$ ) from the first section. The spectroscopic constants for this curve are given in Table 8 along with the experimentally observed frequency of Flyholder and Allen (1965). The agreement is more than likely fortuitous, considering all the approximations made about geometries and so forth, but the implications can not be overlooked by any means.

The qualitative features of our two-orientation proposal are certainly supported by our calculations. Although there is a number of ways we could improve the calculations, one

Figure 12. Calculated potential energy curves for nitric oxide ( $\Delta$ ) and nitric oxide on nickel(100) surface (\*).

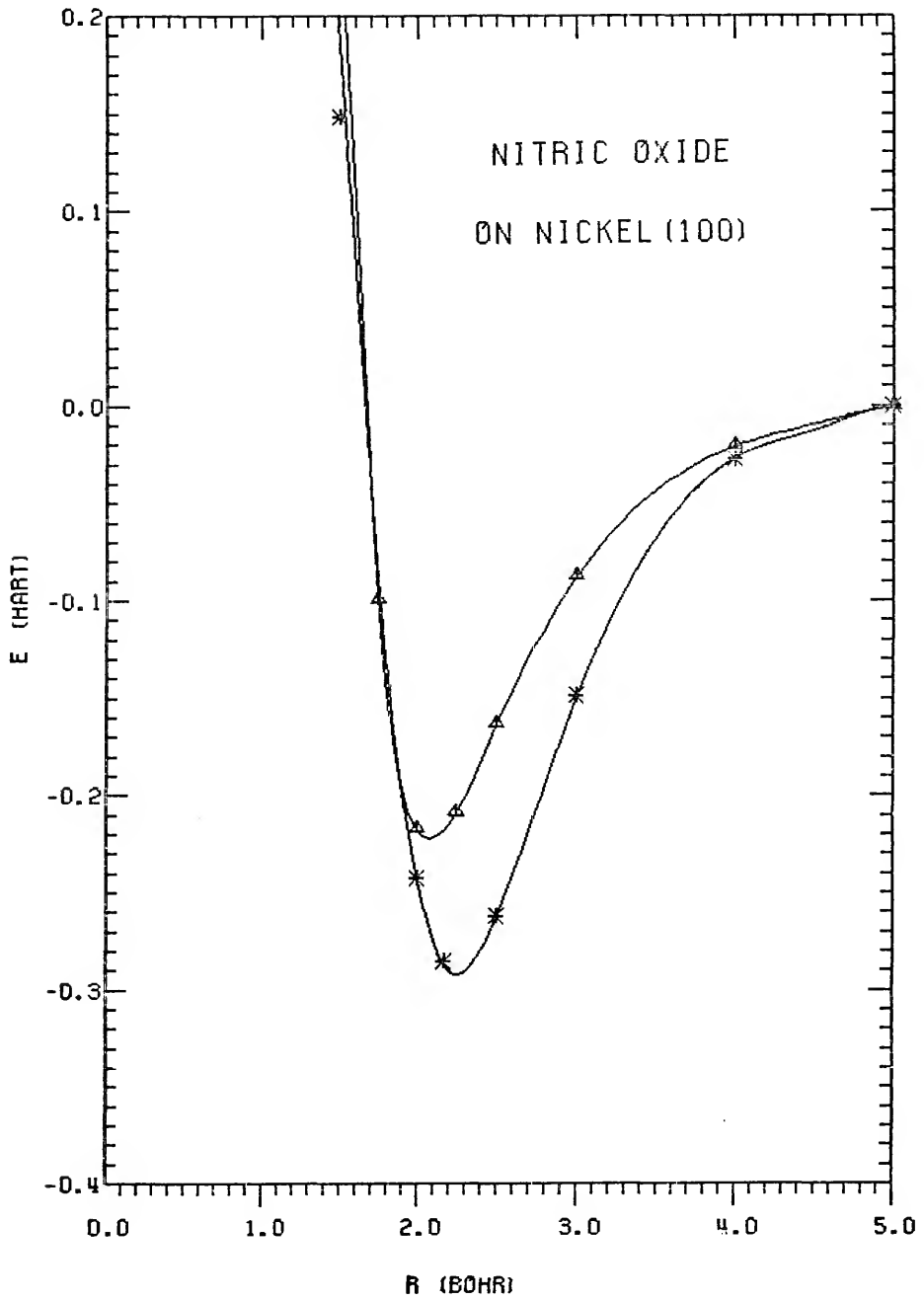




Table 8. Calculated spectroscopic constants for nitric oxide on nickel (100) surface. (oxygen bonded).

Constant	calc
$r$ ( $\text{\AA}$ )	1.19
$\epsilon$	
$w$ ( $\text{cm}^{-1}$ )	2186
$\epsilon$	
$w_x$ ( $\text{cm}^{-1}$ )	19
$\epsilon$	
$B$ ( $\text{cm}^{-1}$ )	1.59
$\epsilon$	
$\alpha$ ( $\text{cm}^{-1}$ )	0.024
$\epsilon$	
$D$ (eV)	7.97
$\epsilon$	
$E(0 \rightarrow 1)$ ( $\text{cm}^{-1}$ )	2148 (2205) <sup>a</sup>

<sup>a</sup> Experimentally observed frequency of Blyholder and Allen (1965).

doubts that such quantitative proof can ever be presented for such a complex system. We have not, for instance, even considered the interactions of the other molecules on the surface (one in every hole site most likely, from intensity estimates). Temperature and concentration (pressure) were key factors in the experiments and these effects are definitely outside the range of our current quantum-theoretic tools. The ultimate goal, of course, is to be able to describe the chemistry which takes place "on" the

surface and to discern the explicit role of the surface on a quantum mechanical level. As a first step, one must be able to characterize the various species which might exist during the course of such a reaction, for only then can one begin to look at the dynamics involved. We feel that a method capable of such characterization is nearly at hand and that potential energy surfaces for such complex reactions are just around the corner. Each day, more and more experimental information about the chemisorption process becomes available, just as more and more stumbling blocks are being eliminated in the quantum mechanical treatment. We hope that the present account has supplied credible evidence that the road to understanding the catalytic nature of the chemisorption process on a quantum mechanical level is now being cleared.

CHAPTER X  
DISCUSSION

The method we have tried to present here is still in a youthful stage of its development, having been conceived, given vitality in the ever-amendable form of computer software, and ready to withstand the test of time. Its maturity will most certainly come only with growth and inevitable change, for nearly every assumption or approximation that has been made in its early stages can be improved upon to some extent if necessary. Before one can make much constructive (or destructive, for that matter) criticism, though, the method needs considerable testing. Our primary aim here was to present an application which demonstrates its applicability to a variety of systems. Such a study, however, does not produce any trends or provide any statistics by which to judge its predictability or its reliability. Studies in this regard are, of course, forthcoming and should prove to be indicative of any need for alterations in the method.

It would be worthwhile, perhaps, to review the assumptions and approximations which are to be placed under such scrutiny. The most fundamental approximation, outside the independent-particle model, that must be examined carefully for its justification is the use of the Mulliken approximation at various stages. It was the use of this approximate form of the differential overlap (accurate to second-order in diatomic overlap) which allows for the replacement of the constrained eigenfunctions by their renormalized unconstrained counterparts. And this is what leads to the single-centered expansions. The next approximation which comes to mind is the Hermitean truncated (through second-order in overlap) expansion of the energy-dependent part of the pseudopotential. The question here is one more of validity than of accuracy, insofar as the Hermiticity is concerned. The integral approximations are perhaps the easiest to criticize, but these approximations are rather straightforward and can be improved if the need is indicated. The model Hamiltonian used to obtain molecular orbitals is perhaps the most disputable aspect of our treatment. The problem is not so much with the molecular orbitals or energies themselves but rather with the subsequent population analysis which one would like to employ in the self-consistent charge and configuration procedure. This can be a crucial point if one wishes to describe states which require heavy mixing of

configurations. One might hope that a diabatic single-configuration state in terms of localized orbitals is the closest model of a real physical situation, and that such a self-consistent procedure would not, in general, be necessary. This subject could comprise a treatise of its own, so we omit any further discussion here. The treatment of spin in our unrestricted approach can also be debated at great length and a proper discussion could not be contained here. These last two points are quite dependent upon one's own interpretation of a real chemical situation in relation to what is a proper treatment of spin, symmetry, and so forth; and only further testing will bear this out. This type of discourse should probably be reserved for more suitable circumstances. One point which has not been mentioned so far is the applicability of the method to large atoms. This, of course, entails careful concern for relativistic effects, as well as for the increased dimensionality. An attractive recourse here would be the use of core pseudopotentials which incorporate relativistic corrections (Das and Wahl, 1976). Such adaptations, as well as the inclusion of various spin interactions directly into the Hamiltonian, are currently under consideration.

To reiterate, all of these points demand further testing before much can be said in their defense or otherwise. Let us end this report of a new and promising approach to the

study of polyatomic systems, as though it really were in its youth and eagerly awaiting its chance to prove itself in a world which is equally anxious for the arrival of such a method.

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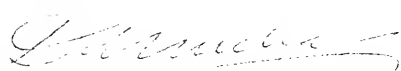
## BIOGRAPHICAL SKETCH

Jack A. Smith was born October 16, 1949, in Indianapolis, Indiana. He graduated from Arlington High School at Indianapolis in June, 1967. In June, 1971, he received the degree of Bachelor of Science with majors in chemistry and mathematics from Indiana University - Purdue University at Indianapolis. In September, 1971, he enrolled in the Graduate School at the University of Florida. In August, 1972, he joined the Quantum Theory Project at the University of Florida. In December, 1973, he received the degree of Master of Science in chemistry. Since that time he has pursued the degree of Doctor of Philosophy at the University of Florida and is presently still a member of the Quantum Theory Project. On July 3, 1976, he married the former Miss (Susan) Malissa Brockett.

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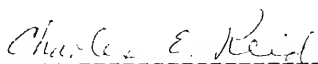
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