THEORETICAL STUDIES OF CHEMISORPTION ON TRANSITION METAL SURFACES:
INTERACTION OF HYDROGEN WITH TITANIUM*

PROGRESS REPORT
FOR PERIOD JUNE 1, 1977 - MAY 31, 1978

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Theoretical Studies of Chemisorption on Transition Metal Surfaces:

Interaction of Hydrogen with Titanium

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Summary

The research is concerned with the theory of chemisorption of molecules on solid surfaces, with applications to the hydrogen-titanium system. The ab initio computational formulation is based on two main ideas: (1) the application of a recently developed approximation technique which utilizes error bounds on electrostatic interactions to achieve a major organizational simplification of the problem, and (2) the definition of a local (surface) region plus the adsorbate in which the partitioning is accomplished by an orbital localization scheme.

The first phase of research was concerned primarily with the implementation of basic computational techniques including the approximation of electrostatic interactions, development of multipole expansions, and the direct approximation of the electron density and first order density matrix derived from a given wavefunction based on error bound criteria. A pseudopotential method was developed for the approximation of atomic cores.

Calculations on Ti atom, TiH, Ti_n -linear ($n = 1-10$), Ti_9 -planar, and Ti_9H systems were carried out to test the computational methods and to examine the concept of a local (surface) region defined by the localization transformation. In all linear chain and Ti_9 -planar cases, the exchange maximization with a designated site gave well localized orbitals, and in the linear chains, the localized orbitals were found to be invariant for $n \geq 4$.

Theoretical Studies of Chemisorption on Transition Metal Surfaces:
Interaction of Hydrogen with Titanium*

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Annual Progress Report**

The research is concerned with the theory of chemisorption of molecules on solid surfaces, and is directed toward the development of a theoretical model for treating electronic interactions at an ab-initio level. Applications to the hydrogen-titanium system are considered, in which the objective is to obtain a detailed account of molecule-surface interactions, including an adequate response of the lattice to the incoming adsorbate and the likelihood that the adsorption of H_2 Ti(solid) is dissociative. The computational formulation is based on two main ideas: (1) the application of a recently developed approximation technique which utilizes error bounds on electrostatic interactions to achieve a major organizational simplification of the problem, and (2) the definition of a local (surface) region involving the adsorbate and a relatively small cluster of atoms imbedded in a fixed field of a larger cluster of atoms. The partitioning into regions is accomplished by an orbital localization scheme which incorporates directly into the definition of the local region essential characteristics of the initially delocalized description of the lattice (cluster).

In the following, topics of investigation and accomplishments in the first phase of the research are outlined briefly.

1. An electron repulsion integral approximation technique based on rigorous error bounds on integrals is combined with a multipole expansion approximation. These two methods cover both exchange and coulomb type integrals and are particularly effective in the approximation of long range interactions.

2. Translational symmetry has been introduced to simplify further the integral computation step. Since the technique works best for the short range interactions, it complements the integral approximations.

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3. Approximation methods dealing directly with the first-order density matrix are shown to reduce the computational work in the construction of the Fock matrix. Interatomic densities are projected onto atomic one center densities, using error bound criteria, thus replacing the quadratic dependence of the density matrix on the basis functions by a linear one. The approximation is most accurate in the projection of coulombic and localized exchange-self energy densities, as well as in the expansion of atomic cores.

4. A pseudopotential method based on the frozen core approximation and explicitly orthogonalized valence orbitals is shown to provide an accurate description of the core electron field. The inclusion of the valence-core interactions is accomplished by the density matrix expansions.

5. Calculations on Ti atom, TiH, Ti_n - linear ($n = 1-10$), Ti_9 - planar, and Ti_9H systems were carried out to test the computational methods and to examine the concept of a local (surface) region defined by the localization transformation. In all linear chain and Ti_9 - planar cases, the exchange maximization with a designated site gave well localized orbitals, and in the linear chains, the localized orbitals were found to be invariant for $n \geq 4$.

Appendices I and II (attached) of the current research proposal provide detailed information on topics 1, 3 and 5; summaries of the calculations are given in Tables 1-5 and Figures 1-3 (attached).

Table 2. CI calculations on TiH.

State	Energy ^a (a.u.)	R_e (Å)	Energy ^b (a.u.)	R_e (Å)
$^4\Delta$	0.01315	1.90	0.01559	1.95
$^4\Pi$	0.00808	1.86	0.01254	1.89
$^4\Sigma$	0.00497	1.84	0.00296	1.86
$^4\Phi$	0.0	1.84	0.0	1.86

a) Ref. 44 b) basis B8

Table 3. Comparison of Ti₂ valence orbital energies (a.u.) obtained from an explicit core calculation and from a pseudopotential calculation.

Orbital	Explicit core	Pseudopotential
π_u^a	-0.448	-0.438
π_g^a	-0.420	-0.407
σ_g^a	-0.279	-0.277
σ_g^b	-0.261	-0.257
σ_u^a	-0.152	-0.145
σ_u^b	-0.138	-0.128

Table 1. Ti atom ($s^2 d^2, ^3F$) total energy and orbital energies for various basis sets.

	a*	b	c	d	e	f	g
Total energy	-848.2001	-848.1017	-847.8790	-847.8396	-847.8765	-847.8396	-3.2604**
Basis set	A	B	C	C	C	C	C
Orbital energies							
1s	-183.254	-183.236	-183.197	-183.372	-183.208	-183.372	
2s	-21.410	-21.395	-21.277	-21.351	-21.297	-21.367	
2p	-17.764	-17.772	-17.749	-17.818	-17.766	-17.832	
3s	-2.862	-2.859	-2.849	-2.860	-2.912	-2.923	
3p	-1.779	-1.772	-1.784	-1.793	-1.802	-1.890	
3d	-0.424	-0.413	-0.412	-0.418	-0.412	-0.418	-0.418
4s	-0.217	-0.217	-0.197	-0.198	-0.205	-0.205	-0.205
					-0.190	-0.191	-0.191
core	free	free	free	frozen	free	frozen	pseudopot.
SCF method	RHF	RHF	RHF	RHF	SUHF	SUHF	SUHF

* Ref 43.

** valence energy

Table 3. Comparison of the six lowest states of Ti_2 obtained from CI calculations based on explicit and pseudopotential core orbitals.

The energies (a.u.) are relative to the lowest state.

State	Explicit core	Pseudopotential
1	0.0	0.0
2	0.0463	0.0460
3	0.1059	0.1060
4	0.1587	0.1587
5	0.1599	0.1588
6	0.1882	0.1814

Figure 1. The eigenvalue spectrum of linear Ti chains. Connected levels are α and β s-type orbitals, other levels are d-type α orbitals.

Figure 2. Exchange eigenvalues γ of the localized orbitals as a function of the chain length.

a) end atom localization

b) two end atom localization

Table 4. Mulliken populations of the localized Ti_5 s orbitals.

a) End atom localization (one orbital)

b) Two end atom localization (two orbitals)

Center	1	2	3	4	5
Population a	0.932	0.051	0.001	0.008	0.002
Population b	0.920	0.735	0.272	0.048	0.024

Table 5. Configuration interaction results for Ti_5 linear.

Symmetrized d_6 orbitals

$$a = d_2 + d_4$$

$$b = d_3$$

$$c = d_2 - d_4$$

$$d = d_1 + d_5$$

$$e = d_1 - d_5$$

Notation: Configurations $A|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3\bar{\phi}_3\phi_4\bar{\phi}_4xy| = |xy|$

ϕ_1, ϕ_2, ϕ_3 and ϕ_4 are s molecular orbitals.

State	Energy(eV)	Major configurations
1	0.0	$ a\bar{c} $
2	0.21	$ a\bar{b} $
3	0.24	$0.43 a\bar{c} + 0.85 c\bar{b} $
4	1.20	$ d\bar{b} $
5	1.20	$ e\bar{b} $

Figure 3. The eigenvalue spectrum of $T1g$ (left) and $T1gH$ (right)

Electron Density and Density Matrix Approximations
Using Potential Energy Error Bounds

by

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Abstract

The possibility of simplifying expansions of the total electron density, $\rho(1)$, and the first order density matrix, $\gamma(1,1')$, derived from a given total wavefunction is considered based on the minimization of positive definite error bound integrals, $\epsilon_\rho = \langle \rho(1) - \rho'(1) | v_{12} | \rho(2) - \rho'(2) \rangle$ and $\epsilon_\gamma = \langle \gamma(1,2) - \gamma'(1,2) | v_{12} | \gamma(1,2) - \gamma'(1,2) \rangle$. Expansions, ρ' and γ' , are in terms of a subset of the full basis and are designed for iterative use in energy variational calculations. In all of a variety of cases investigated, simple one-center expansions are found to be very accurate for the ρ expansion which determines the total coulombic energy of the system. However, correspondingly simple, one-center $\gamma(1,2)$ expansions produce significant errors in the exchange, self-energy when the electron distribution is highly delocalized requiring that important two-center distributions be included for accurate calculations. Applications to localized electron distributions and to problems in which a lower level of accuracy is acceptable are discussed.

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I. Introduction

Ab initio electronic structure calculations generally employ basis set expansions of the single particle functions used in the construction of total wavefunctions. In energy computations, assuming N basis functions, there occur on the order of $\frac{N^4}{8}$ electron repulsion integrals; thus, when large basis sets are used, calculations can become lengthy at both the integral evaluation and integral processing stages. A great deal of work has been reported on the evaluation and approximation of electron repulsion integrals,^{1,2} and in a recent series of papers, it was shown that useful approximation methods could be developed from a simple error bound derivable from electrostatics.³ Introducing the notation,

$$\langle g_1(1)g_j(1) | r_{12}^{-1} | g_k(2)g_l(2) \rangle = \langle \phi_{ij} | v_{12} | \phi_{kl} \rangle$$

where g denotes an arbitrary basis function, a bound on the difference between exact and approximate integrals was developed such that

$$|\langle \phi_{ij} | v_{12} | \phi_{kl} \rangle - \langle \phi'_{ij} | v_{12} | \phi'_{kl} \rangle| \leq \delta$$

where δ is known and ϕ'_{ij} and ϕ'_{kl} are approximations of the electron densities ϕ_{ij} and ϕ_{kl} . The attractiveness of the approach is due to the simple structure of the bound δ which depends only on information calculated separately for the pair of densities ϕ_{ij} and ϕ'_{ij} , and the pair ϕ_{kl} and ϕ'_{kl} , and the fact that density approximations can be generated by minimization of δ .

Previous applications were concerned with the approximation of individual integrals over basis functions and the subsequent use of these integrals in energy variational calculations. In the present work, we consider the first order density matrix derived from a proposed wavefunction and the approximation of integrals involving the density matrix or the total electron density directly.

Single-determinant, closed-shell self-consistent-field (SCF) wavefunctions are assumed throughout, but the extension to an unrestricted Hartree-Fock level is trivial. Applications to configuration interaction wavefunctions seem possible in principle but are not considered in this work. As will be seen, very simple applications of the theory to the approximation of the total coulombic energy of a system are remarkably successful, but at a correspondingly simple level of treatment the exchange, self-energy approximation shows a much larger error, although one which is tolerable for certain purposes.

II. Theory

The total energy of a system of $2M$ electrons described by a single-determinant total wavefunction of M doubly occupied, orthonormal spatial orbitals, φ_i , can be written

$$E = \sum_i^M 2 \langle \varphi_i(1) | h_1 | \varphi_i(1) \rangle + \sum_i^M \sum_j^M \langle \varphi_i(1) \varphi_j(2) | v_{12} | 2\varphi_i(1) \varphi_j(2) - \varphi_i(2) \varphi_j(1) \rangle$$

for a one-electron operator h_1 and interelectronic repulsion potential $v_{12} = r_{12}^{-1}$.

Defining the first order density matrix, assuming real orbitals,

$$\gamma(1,1) = 2 \sum_{i=1}^M \varphi_i(1) \varphi_i(1)$$

and the total electron density

$$\rho(1) = \gamma(1,1) = 2 \sum_{i=1}^M \varphi_i(1) \varphi_i(1)$$

gives the energy as a functional

$$E = \int h_1 \gamma(1,2) dx_1 + \frac{1}{2} \int \rho(1) \rho(2) v_{12} dx_1 dx_2 - \frac{1}{4} \int [\gamma(1,2)]^2 v_{12} dx_1 dx_2$$

If the molecular orbitals φ_i are expanded in terms of N basis functions

$$\varphi_i = \sum_k^N c_{ik} \bar{\epsilon}_k$$

then

$$\gamma(1,2) = 2 \sum_{i=1}^M \sum_{k=1}^N \sum_{l=1}^N c_{ik} c_{il} g_k(1) g_l(2) = 2 \sum_{k=1}^N \sum_{l=1}^N w_{kl} \bar{\epsilon}_k(1) \bar{\epsilon}_l(2)$$

$$w_{kl} = \sum_{i=1}^M c_{ik} c_{il}$$

The exact first order density matrix, $\gamma(1,2)$, thus contains N^2 distributions $g_k(1)g_l(2)$. In the following, we consider the possibility of a simplifying approximation of $\gamma(1,2)$, either through the use of an auxiliary basis set or the projection of less important distributions onto the major ones. In principle, it is only $\gamma(1,2)$ that requires expansion since $\rho(1) = \gamma(1,1)$; however, in practice accurate expansions for $\gamma(1,2)$ are found to be more difficult to achieve than for $\rho(1)$, and therefore the expansions are considered separately.

The approximation criteria considered here are based on minimization of the positive, definite error bound integrals³

$$\epsilon_\rho = \langle \rho(1) - \rho'(1) | v_{12} | \rho(2) - \rho'(2) \rangle$$

$$\epsilon_\gamma = \langle \gamma(1,2) - \gamma'(1,2) | v_{12} | \gamma(1,2) - \gamma'(1,2) \rangle$$

where the approximate densities, $\rho'(1)$ and $\gamma'(1,2)$, are to be determined. In terms of the exact and approximate densities, the energy becomes

$$E = \int h_1 \gamma(1,2) dx_1 + \int \rho'(1) \rho(2) v_{12} dx_1 dx_2 - \frac{1}{2} \int \rho'(1) \rho'(2) v_{12} dx_1 dx_2$$

$$- \frac{1}{2} \int \gamma'(1,2) \gamma(1,2) v_{12} dx_1 dx_2 + \frac{1}{4} \int \gamma'(1,2) \gamma'(1,2) v_{12} dx_1 dx_2$$

$$+ \frac{1}{2} \epsilon_\rho - \frac{1}{4} \epsilon_\gamma$$

If the ϵ_Y term is omitted an upper bound to the true variational energy is still obtained, and if the remaining part of the energy expression is minimized with respect to variations of $\gamma'(1,2)$ the minimization of E condition is clearly identical to that for minimization of ϵ_Y . Similar remarks apply to the determination of $\rho'(1)$ except an upper bound is not obtained on neglect of the ϵ_p term. Another alternative for determining ρ and γ expansions would be to minimize the variances $\langle(\rho-\rho')^2\rangle$ and $\langle(\gamma-\gamma')^2\rangle$, but the present approach based on ϵ_p and ϵ_Y has the advantage of being directly related to the energy of the system.

The basis used to expand γ' can be chosen independently of the basis used to define the exact density matrix, but the functions must be such that the integrals $\langle\gamma(1,2)|\psi_{12}|\gamma'(1,2)\rangle$ and $\langle\gamma'(1,2)|\psi_{12}|\gamma(1,2)\rangle$ can be evaluated; likewise, the ρ' and ρ bases can be chosen independently. In addition, the Fock operator requires integrals of the type $\langle g_i(1)g_j(2)|\psi_{12}|\gamma'(1,2)\rangle$ and $\langle g_i(1)g_j(1)|\psi_{12}|\rho'(2)\rangle$ which are the same as occur also as components of the γ , γ' and ρ , ρ' interaction integrals. It should be noted that the extrema conditions for the determination of γ' and ρ' do not require a knowledge of the exact-exact interactions, $\langle\gamma(1,2)|\psi_{12}|\gamma(1,2)\rangle$ and $\langle\rho(1)|\psi_{12}|\rho(2)\rangle$. However, in order to make practical use of this result, it must be known from other considerations that the γ' and ρ' expansions are sufficiently flexible to guarantee small ϵ_Y and ϵ_p .

In the present work we consider only one type of ρ' and γ' expansion such that the γ' basis is a subset of the basis used to expand the exact γ , and similarly for the ρ' basis; that is, we consider only approximations derived by projecting the less significant distributions into the major distributions. Two levels of treatment are considered as follows:

1) Projection of two-center distributions onto single-center distributions

$$\rho'(1) = \sum_A \sum_{k,l}^{\text{atoms } eA} x_k(1)x_l(1)\lambda_{kl}$$

$$\gamma'(1,2) = \sum_A \sum_{k,l}^{\text{atoms } eA} x_k(1)x_l(2)\lambda_{kl}$$

Further simplified expansions are also investigated by projecting one-center k , l distributions onto k , k distributions.

2) Selective projection of two-center distributions onto single-center distributions

$$\rho'(1) = \left[\sum_A \sum_{k,l}^{\text{atoms } eA} x_k(1)x_l(1)\lambda_{kl} \right] + \sum_{k,l}^{eS} x_k(1)x_l(1)\lambda_{kl}$$

$$\gamma'(1,2) = \left[\sum_A \sum_{k,l}^{\text{atoms } eA} x_k(1)x_l(2)\lambda_{kl} \right] + \sum_{k,l}^{eS} x_k(1)x_l(2)\lambda_{kl}$$

where S denotes selected two-center distributions included in the expansions.

The former expansion is formally exact if the delocalized orbitals c_i can be completely localized by a unitary transformation, but otherwise a projection of two-particle, two-center distributions onto single-center distributions is required. The latter expansion allows for the possibility that a selected number of the two-center distributions cannot be projected accurately onto single-center distributions. Computationally it is more time consuming, and if all k , l distributions were included the latter expansion would become exact. It should be noted that one-center ρ projections of type (1) are known to be often inaccurate if determined by maximum overlap projection, however, the error bound theory provides a very different context for the analysis.

Coefficients λ_{ij} in all expansions are determined by minimizing ϵ_p and ϵ_y in separate calculations, with respect to λ_{ij} . For the p expansion,

$$\frac{\partial \epsilon_p}{\partial \lambda_{ij}} = 0$$

gives

$$\langle \rho'(1) - \rho(1) | v_{12} | \frac{\partial \rho'(2)}{\partial \lambda_{ij}} \rangle = 0$$

which is a set of simultaneous linear equations in λ_{ij} . For the solution set of λ_{ij} , ϵ_p becomes

$$\epsilon_p = \langle \rho(1) | v_{12} | \rho(2) \rangle - \langle \rho'(1) | v_{12} | \rho'(2) \rangle$$

Similarly for the $y(1,2)$ expansion, $\frac{\partial \epsilon_y}{\partial \lambda_{ij}} = 0$ gives

$$\langle y'(1,2) - y(1,2) | v_{12} | \frac{\partial y'(1,2)}{\partial \lambda_{ij}} \rangle = 0$$

and for the solution set of λ_{ij}

$$\epsilon_y = \langle y(1,2) | v_{12} | y(1,2) \rangle - \langle y'(1,2) | v_{12} | y'(1,2) \rangle$$

The above systems of equations can be solved by standard matrix inversion methods, but in certain cases the matrix can be nearly singular. In such a case, and in fact in all cases, it was found convenient to proceed by orthogonalizing the products of basis functions $x_k x_l$ by a Gram-Schmidt procedure using $v_{12} = r_{12}^{-1}$ as a weighting factor.

Thus, letting $\phi_m = x_k(1)x_l(1)$ for the p case, define

$$\phi_1' = A_1 \phi_1$$

$$\phi_2' = A_2 [\phi_2 - \langle \phi_1'(1) | v_{12} | \phi_2(2) \rangle \phi_1']$$

...

$$\phi_m' = A_m [\phi_m - \sum_l \langle \phi_l'(1) | v_{12} | \phi_m(2) \rangle \phi_l']$$

where the factors A_m are chosen such that $\langle \phi_m'(1) | v_{12} | \phi_m'(1) \rangle = 1$. The $\rho'(1)$ expansion then becomes

$$\begin{aligned} \rho'(1) &= \sum_{ij} \lambda_{ij} x_i(1) x_j(1) \\ &= \sum_{ij} \lambda_{ij}' (x_i x_j)' \end{aligned}$$

where $(x_i x_j)'$ denotes the v_{12} weighted orthogonalized product distributions ϕ_m' , and $\epsilon_p = \langle \rho(1) | v_{12} | \rho(2) \rangle - \sum_{ij} \lambda_{ij}'^2$. The orthogonalization method thus allows an easy estimate of the contribution of a distribution to ϵ which is an aid in the selection of an effective expansion basis. Equations of the same form are obtained for the y' expansion except everywhere two particle distributions, $x_k(1)x_l(2)$, occur and integrals are of the form $\langle \phi_m(1,2) | v_{12} | \phi_n(1,2) \rangle$.

As noted earlier, evaluations of $\langle \rho | v_{12} | \rho \rangle$ and $\langle y | v_{12} | y \rangle$ are not required to determine the expansions, but would be required to calculate the errors. The dependence is on the order of M^3 integrals, in principle, where M is the number of basis functions, but in practice the number of required integrals is greatly reduced due to the rapid diminution of integrals with increasing distance between basis functions.

III. Numerical Tests

In order to investigate the accuracy of the electron density and density matrix expansions discussed in the previous section, calculations were carried out on three different types of electron distributions: the diatomic molecules N_2 and CO, a lattice of 36 hydrogen atoms and the core electrons of the titanium atom. Each system places a somewhat different demand on the expansion theory. In N_2 and CO, the molecules exhibit strong bonding of the valence electrons, but with a two-center delocalized distribution. The H_{36} lattice exemplifies a highly delocalized electronic system, and in Ti the core electrons form a highly localized distribution with large coulombic repulsion. In each case the exact reference calculation is for a density matrix derived from a converged closed-shell SCF wavefunction.

Table I. shows the results of ρ and γ expansions for N_2 and CO. Values for ϵ_ρ and ϵ_γ are reported for each choice of expansion along with the number of pairs $\chi_k(1)\chi_k(2)$ present in the approximate expansion. The latter number gives a measure of the degree of simplification achieved by the approximations, but for these diatomic molecules with the present basis this cannot be extensive since the fraction of one-center distributions is ~ 0.2 . It is evident from the results in Table I. that the ρ -expansions work remarkably well. The $\chi_k(1)\chi_k(1)$ one-center expansion captures all but 0.02% of the total coulombic energy while inclusion of the one-center cross terms $\chi_k(1)\chi_k(1)$ lowers the deviation to $3 \times 10^{-4}\%$ for N_2 and $1 \times 10^{-4}\%$ for CO. The greater improvement for CO is a consequence of the slightly greater atomic localization in that molecule compared to N_2 .

In contrast the γ expansions are much less satisfactory. Expansions B and E in Table I. in which all two-center distributions are projected onto one-center

distributions of the type $\chi_k(1)\chi_k(2)$ have ϵ_γ values of 0.187 and 0.123 for N_2 and CO respectively. Since ϵ_γ is the difference between the exact and approximate exchange, self-energy,

$$\epsilon_\gamma = \frac{1}{2} \left[\langle \gamma(1,2) | v_{12} | \gamma(1,2) \rangle - \langle \gamma'(1,2) | v_{12} | \gamma'(1,2) \rangle \right]$$

these values correspond to underestimates of this interaction; the exact exchange, self energy is ~ 13 a.u. in both molecules. In view of the simplicity of the approximation deviations of this order are not surprising, but certainly the error precludes an accurate calculation of the energy at this level of approximation. The effect of mid-bond basis functions was also studied, and the results show that the expansions cannot be improved in this way; inclusion of medium range s and p functions reduced ϵ_γ by only 3%.

It is evident from the numerical results on N_2 that the two-center valence orbital distributions in $\gamma(1,2)$ are not adequately described by the one-center projection, whereas this was not the case in the ρ expansion. As noted previously, for the highly localized core orbital distributions the $\gamma(1,2)$ one-center expansion must approach the exact. In order to examine the relative contributions to ϵ_γ , $\gamma(1,2)$ can be divided into core and valence contributions, γ^c and γ^v , respectively

$$\gamma(1,2) = 2 \sum_1^{\text{core}} \phi_1(1)\phi_1(2) + 2 \sum_1^{\text{val}} \phi_1(1)\phi_1(2) = \gamma^c(1,2) + \gamma^v(1,2)$$

The approximation $\gamma'(1,2)$ can be determined separately for the core and valence contributions, and it can be shown that the sum of the separately determined γ'^c and γ'^v is exactly the optimum total γ' ; see Appendix I. Expanding ϵ_γ for $\gamma = \gamma^c + \gamma^v$ and $\gamma' = \gamma'^c + \gamma'^v$ gives

$$\begin{aligned} \epsilon_\gamma &= \langle \gamma | v_{12} | \gamma \rangle - \langle \gamma' | v_{12} | \gamma' \rangle \\ &= \epsilon_\gamma^c + \epsilon_\gamma^v + 2[\langle \gamma^c | v_{12} | \gamma^v \rangle - \langle \gamma'^c | v_{12} | \gamma'^v \rangle] = \epsilon_\gamma^c + \epsilon_\gamma^v + \epsilon_\gamma^{c-v} \end{aligned}$$

Table II. gives the contributions to ϵ_V for N_2 for the simplest one-center projection of the form $\chi_K(1)\chi_K(2)$, and for a core of $1\sigma_g$ and $1\sigma_u$ orbitals. It is clear that the simplest expansion works well for the core distribution and for the small core-valence exchange interaction; however, there is a significant error in representing the valence distribution. The error can be reduced by inclusion of selected major two-center distributions $\chi_K(1)\chi_L(2)$ in $\gamma'(1,2)$; Expansion C of Table I. shows a much smaller $\frac{1}{4}\epsilon_V$ of 0.036 a.u., but this is at the expense of increasing the number of distributions in the expansion to 68 out of a possible total of 98 for the present basis.

The next system considered is that of a cubic lattice of 36 hydrogen atoms consisting of four layers of atoms, 9 atoms/layer. In this case, the SCF solution yields highly delocalized molecular orbitals extending over the entire lattice. Thus, the system is one for which a one-center projection of the density matrix would be expected to show a large error. Table I. shows that this is indeed the case for Expansion F for which the errors are $\frac{1}{2}\epsilon_p = 0.132$ a.u. and $\frac{1}{4}\epsilon_V = 5.65$ a.u. out of a total coulombic energy of 201.3 a.u. and an exchange, self-energy of 13.6 a.u. Clearly only about one-half of the exchange, self-energy is accounted for by the projection. Including in the γ' expansion the nearest neighbor distribution $g_K(1)g_L(2)$, where g_K and g_L are functions on adjacent nuclei, produces a large improvement reducing $\frac{1}{4}\epsilon_V$ to 1.15 a.u. However, not much of an improvement occurs on going to the next nearest neighbor distribution, and thus in this highly delocalized example many non-negligible distributions lie outside the space spanned by one-center, nearest neighbor, and next nearest neighbor distributions. In a more optimistic sense, it is noted that the error is on the order of 0.03 a.u. per hydrogen atom, and the possibility that this is a tolerable error for certain purposes is considered in a subsequent section.

It is clear from the foregoing data that in calculations of high accuracy the $\gamma(1,2)$ one-center expansions could not be employed when extensive orbital delocalization exists. Furthermore, the results on the hydrogen lattice demonstrate that the successive addition of selected two-center distributions does not necessarily produce a rapid improvement in the expansion. The fault lies in the nature of the two-particle, two-center distribution. Distributions such as $g_A(1)g_B(2)$, where A and B denote different origins, can contribute to major coulombic repulsion interactions, such as the self-interaction, $(g_A(1)g_B(2)|\psi_{12}|g_A(1)g_B(2))$, or interactions with distributions $g_A(1)g_A(2)$ or $g_B(1)g_B(2)$. It follows that the approximation of $g_A(1)g_B(2)$ by a one-center projection can produce a significant error. In contrast, in the more successful p expansion, projection of $g_A(1)g_B(1)$ leads to an ϵ_p of the exchange integral type as opposed to the coulombic nature of ϵ_V on projection of $g_A(1)g_B(2)$.

Of course, if it is known that part of the density matrix is due to a localized electron distribution, then a reasonable approach would be to employ a one-center expansion for that part of $\gamma(1,2)$ and to make few if any approximations in the remainder. Core expansions of atoms certainly fall into this category. In addition, in certain systems, localized orbitals can often be predicted to exist at the outset, as for example, the localized d orbitals in clusters of transition metal atoms. To illustrate this type of application, consider a calculation on Ti_2 where $\gamma(1,2)$ was projected onto one-center atomic distributions except for the diffuse $4s$ orbital distribution, $s_A(1)s_B(2) + s_A(2)s_B(1)$, where A and B denote different nuclei, which was retained explicitly in the expansions; the resulting error, $\frac{1}{4}\epsilon_V$, in the exchange, self-energy was found to be only ~ 0.01 a.u.

The present expansion theory based on ϵ_p and ϵ_V minimization is also well-suited

to the problem of determining an effective coulomb and exchange potential of atomic core electrons for subsequent use in a pseudopotential theory. In the following, the titanium atom is considered as an example, and the core electron density is expanded as a linear combination of spherical gaussian functions. The Ti core is taken as $1s^2 2s^2 2p^6 3s^2 3p^6$, where in the present basis the s and p orbitals have 12 and 6 gaussian components, respectively, which gives an exact ρ_{core} containing 330 products of single Gaussians. Table III. shows that the accuracy of the ρ expansion is excellent for a relatively small number of gaussians, e.g., as few as 9 components. Also reported in the Table is a result for a $1s^2 2s^2 2p^6$ core and for the expansion of a spherically averaged 3d distribution,

$$\rho_{3d} = \sum_{k=1}^5 d_k(1) d_k(1)$$

In order to be useful in SCF calculations, it must be possible to use the ρ and γ expansions iteratively taking the density matrix of the previous iteration to define the exact ρ and γ . Several SCF calculations were performed to study the effect of approximate ρ and γ expansions on the total energy, orbital energies and convergence. Since the ρ and γ expansions differ greatly in quality, they are considered separately. The error, ϵ_{ij} , in the coulombic contribution to a Fock matrix element, F_{ij} , is bounded as follows

$$\epsilon_{ij} = |\langle i(1)j(2) | \frac{1}{r_{12}} | \rho(2) - \rho'(2) \rangle| \leq \epsilon_p^{\frac{1}{2}} \langle i(1)j(1) | \frac{1}{r_{12}} | i(2)j(2) \rangle^{\frac{1}{2}}$$

and similarly for the exchange, self-energy contribution. Thus, it is clear that the accurate ρ expansions in Table I could not significantly distort the SCF solution. In order to demonstrate the effect of an error in ρ , the least accurate expansion for N_2 is considered, viz., Expansion A for which $\frac{1}{2} \epsilon_p = 0.0156$ a.u.

Table IV shows that even this crude ρ expansion reproduces rather well the total energy and orbital energies, and no difficulties in convergence were noted. The differences that do exist are due to a variation of the orbitals in the approximate field as well as a direct error in the use of the approximate ρ in the energy calculation.

In contrast, the use of the simplest $\gamma(1,2)$ expansion for which $\frac{1}{2} \epsilon_\gamma$ is very large, 0.631 a.u., produced large errors in the SCF solution as shown in Table IV. The main effect is in the total energy and an upward shift of the valence orbital energies by ~ 0.1 a.u. As noted previously, it is necessary to retain certain of the two-center valence orbital distributions to achieve a small ϵ_γ in N_2 , and the large error in the full one-center projection precludes its quantitative application. On the other hand, the data support the use of one of the simpler ρ expansions for accurate calculations.

Finally, we consider the application of the simpler type of γ expansion to problems for which a somewhat low level of accuracy is sufficient, for example, a γ expansion for a region of a molecule or portion of a solid lattice that is remote to a site of interest. What is assumed sufficient in this case is an approximate wavefunction and field of the region treated approximately. First it is noted that the exchange, self-energy error is uniformly distributed spatially since the density matrix is projected onto all atomic distributions. Second, the exchange, self-energy field itself is certainly small compared to the coulombic field, and thus, an error in its representation may not lead to a serious distortion of the molecular orbitals. Calculations on the H_{36} lattice, which is the worse case investigated, support this contention: the Fock matrix obtained from a very rough expansion of $\gamma(1,2)$ and an accurate expansion of $\rho(1)$ produced a total wavefunction in good agreement with the

results of an accurate SCF treatment. Table V shows a comparison of exact and approximate virtual orbitals for an SCF calculation on H_{36} using an approximate $\gamma'(1,2)$ expanded uniformly over all sites.

$$\gamma(1,2) = \sum_k \epsilon_k(1)\epsilon_k(2) 2^{-\frac{1}{2}}$$

If the two sets virtual orbitals are in good agreement, as is the case here, it follows that the total wavefunctions are in good agreement even though the individual occupied molecular orbitals may not compare as favorably; i.e., the occupied orbitals are determined only to within a unitary transformation.

IV. Summary

The positive definite error bound integrals, $\epsilon_p = \langle \rho(1) - \rho'(1) | v_{12} | \rho(2) - \rho'(2) \rangle$ and $\epsilon_\gamma = \langle \gamma(1,2) - \gamma'(1,2) | v_{12} | \gamma(1,2) - \gamma'(1,2) \rangle$, provide a useful basis for the determination of approximate expansions of the total electron density, $\rho(1)$, and the first order density matrix, $\gamma(1,2)$, derived from a given total wavefunction. In the present work only very simple expansions are considered in which the basis is a one-center, or one-center plus selected two-center, subset of the full two-particle basis. In all cases investigated, the simple one-center expansions are found to be very accurate for the ρ expansion which determines the total coulombic energy of the system. The correspondingly simple, one-center $\gamma(1,2)$ expansions produce significant errors in the exchange, self-energy when the electron distribution is highly delocalized, requiring in this case the inclusion of at least the important two-center distributions. Applications to core electron potentials and to other localized electron distributions are completely satisfactory, however, at a simple level of treatment. Likewise, in problems in which a lower level of accuracy is acceptable, simple $\gamma(1,2)$ expansions may be applicable in view of the spatial distribution of the error and the fact that the error is small in magnitude compared to the total coulombic repulsion energy of a system.

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Appendix I

Given a basis $\{\delta_k\}$, the coefficients c_k which minimize

$$\epsilon = \langle Y - Y' | v_{12} | Y - Y' \rangle$$

where $Y = Y_c + Y_v$ and $Y' = \sum c_k \delta_k$ can be obtained by independent minimizations of

$$\epsilon_c = \langle Y_c - Y_c' | v_{12} | Y_c - Y_c' \rangle$$

and

$$\epsilon_v = \langle Y_v - Y_v' | v_{12} | Y_v - Y_v' \rangle$$

where $Y_c' = \sum a_k \delta_k$ and $Y_v' = \sum b_k \delta_k$. Proof:

$$\frac{\partial \epsilon}{\partial c_k} = 0 \Rightarrow \tilde{c} = \tilde{w}^{-1} \tilde{v} \text{ where } w_{kl} = \langle \phi_k | v_{12} | \phi_l \rangle$$

$$v_k = \langle \phi_k | v_{12} | Y \rangle$$

$$\frac{\partial \epsilon_c}{\partial a_k} = 0 \Rightarrow \tilde{a} = \tilde{w}^{-1} \tilde{v}^c \text{ where } v_k^c = \langle \phi_k | v_{12} | Y_c \rangle$$

$$\frac{\partial \epsilon_v}{\partial b_k} = 0 \Rightarrow \tilde{b} = \tilde{w}^{-1} \tilde{v}^v \text{ where } v_k^v = \langle \phi_k | v_{12} | Y_v \rangle$$

$$\text{Thus, } \tilde{c} = \tilde{a} + \tilde{b} \text{ Since } v_k = v_k^c + v_k^v$$

Table I. Electron density, $\rho(1)$, and density matrix, $\gamma(1,2)$, expansions for N_2 , CO and H_{36} . The quantities $\frac{1}{2} \epsilon_p$ and $\frac{1}{4} \epsilon_v$ are the errors in the total coulombic energy and exchange, self-energy, respectively.^a

System ^b	Expansion ^c	$\frac{1}{2} \epsilon_p$	$\frac{1}{4} \epsilon_v$	Number of terms in the expansion ^d
A N_2	$\sum_i \lambda_i X_i X_i$	.0156	.631	20
B N_2	atoms ϵ_A $\sum_A \sum_{ij} \lambda_{ij} X_i X_j$	.0002	.187	54
C N_2	atoms ϵ_A ϵ_S $\sum_A \sum_{ij} \lambda_{ij} X_i X_j + \sum_{ij} \lambda_{ij} X_i X_j$	.00005	.036	68
D CO	$\sum_i \lambda_i X_i X_i$	.0177	.587	20
E CO	atoms ϵ_A $\sum_A \sum_{ij} \lambda_{ij} X_i X_j$	.0001	.138	54
F H_{36}	atoms $\sum_i \lambda_i X_i X_i$	0.132	5.65	36
G H_{36}	atoms ϵ_A ϵ_{NN} $\sum_i \lambda_i X_i X_i + \sum_{ij} X_i X_j \lambda_{ij}$	0.003	1.15	111
H H_{36}	atoms ϵ_A ϵ_{NN} ϵ_{NNN} $\sum_i \lambda_i X_i X_i + \sum_{ij} X_i X_j \lambda_{ij} + \sum_{k\ell} X_k X_\ell \lambda_{k\ell}$		1.02	215

^a SCF calculations using the fixed group basis sets of Ref. 5.

^b N_2 coulombic energy, 74.34573 a.u.; exchange, self-energy, 13.0628 a.u.
CO coulombic energy, 75.86845 a.u.; exchange, self-energy, 13.2942 a.u.
 H_{36} coulombic energy, 201.305 a.u.; exchange, self-energy, 13.589 a.u.

^c Nearest neighbor and next nearest neighbor terms are denoted by NN and NNN, respectively.
S denotes selected valence, 2-center distributions.

^d Number of exact distributions is 98 in N_2 and CO, and 666 in H_{36} .

Table II. Analysis of the $\gamma(1,2)$ Expansion of N_2 . Relative contributions of core and valence orbital distributions to ϵ_γ are reported for the simplest $\gamma(1,2)$ expansion, (Expansion A of Table I).^a

$\langle \gamma^c v_{12} \gamma^c \rangle = 8.245^b$	$\epsilon_\gamma^c = 0.033^b$	% Error 0.4
$\langle \gamma^v v_{12} \gamma^v \rangle = 4.387$	$\epsilon_\gamma^v = 0.586$	13
$2 \langle \gamma^v v_{12} \gamma^c \rangle = 0.431$	$\epsilon_\gamma^{c-v} = 0.013$	3
$\langle \gamma v_{12} \gamma \rangle = 13.063$	$\epsilon_\gamma = 0.632$	5

^a Energies are in atomic units.

Superscripts c and v denote core and valence distributions. The full density matrix is $\gamma = \sum \omega_i(1) \phi_i(2) = \gamma^c + \gamma^v$ where the factor of 2 used elsewhere in the definition of γ is omitted; see text for ϵ_γ definitions.

Table III. Titanium atom core electron density expansions,

$\rho(1)$. Approximations $\rho'(1)$ are determined by minimization of

ϵ_ρ (see text) using a basis of simple gaussian functions,

$\rho' = \sum_1 \lambda_i z_i z_1$ where $z_i = N_i \exp(-a_i r^2)$. Energies are in a.u.^a

Core $1s^2 2s^2 3s^2 2p^6 3p^6$, $\langle \rho | v_{12} | \rho \rangle = 623.247$ a.u.

n	ϵ_ρ
3	0.1230
7	0.00167
8	0.000202
9	0.0000963
10	0.0000513
12	0.0000112
16	0.0000039

Core $1s^2 2s^2 2p^6$, $\langle \rho | v_{12} | \rho \rangle = 384.220$ a.u.

n	ϵ_ρ
7	0.0000705

Spherically averaged 3d distribution, $\rho = \sum_{k=1}^5 d_k d_k$, $\langle \rho | v_{12} | \rho \rangle = 64.127$ a.u.

n	ϵ_ρ
2	0.0864
3	0.000436
4	0.000322
5	0.000162
6	0.000127
9	0.000000026

^a The ρ expansions are from a Ti atom SCF calculation using the basis of Ref. 6.

Table IV. Ground state SCF total, E_T , and orbital energies,

ϵ_i , of N_2 obtained using exact ρ and γ expansions and the simplest ρ, γ approximations (Expansion A) of Table I.

	E_T	ϵ_1	ϵ_2	ϵ_3	ϵ_4	ϵ_5	ϵ_6
Exact	-108.8708	-15.716	-15.713	-1.527	-0.774	-0.626	-0.624
Exact γ , Approx ρ .	-108.8887	-15.708	-15.705	-1.481	-0.809	-0.657	-0.617
Exact ρ , Approx γ .	-108.4867	-15.679	-15.678	-1.482	-0.715	-0.539	-0.504

Table V. Comparison of the virtual molecular orbitals of the H_{16} lattice from an SCF calculation using a simple exchange, self-energy approximation^a with the results of a converged SCF calculation based on the accurate evaluation of all integrals.^b

Orbital Coefficients			Orbital Coefficients			Orbital Coefficients		
ϵ	exact	approx	ϵ	exact	approx	ϵ	exact	approx
0.105	0.59	0.59	0.296	-0.28	-0.33	0.968	0.50	0.48
	0.0	0.0		0.79	0.80		-0.11	-0.11
	-0.59	-0.59		-0.44	-0.43		0.50	0.48
	0.0	0.0		-0.18	-0.10		-0.11	-0.11
	0.0	0.0		0.0	0.0		-0.68	-0.70
	-0.38	-0.38		-0.36	-0.39		-0.56	-0.57
0.212	0.51	0.50	0.297	0.0	0.0	1.111	0.39	0.39
	0.10	0.14		0.73	0.73		-0.72	-0.71
	-0.15	-0.10		0.0	0.0		0.39	0.39
	0.19	0.21		-0.73	-0.73		-0.72	-0.71
	0.0	0.0		0.0	0.0		1.22	1.22
	-0.45	-0.51		0.0	0.0		0.51	0.51
0.212	0.15	0.10	0.689	-0.23	-0.20	1.581	0.49	0.44
	0.19	0.21		0.36	0.35		-0.75	-0.75
	0.51	0.50		-0.23	-0.20		0.62	0.62
	-0.10	-0.14		0.36	0.35		0.13	0.12
	0.0	0.0		-0.56	-0.58		0.0	0.0
	-0.13	-0.10		-0.47	-0.48		0.73	0.75
0.262	0.45	0.47	0.830	0.53	0.53	1.66	0.66	0.66
	0.04	0.02		0.0	0.0		-0.93	-0.94
	0.45	0.47		-0.53	-0.53		0.66	0.66
	0.04	0.02		0.0	0.0		-0.93	-0.94
	-1.11	-1.10		0.0	0.0		1.29	1.31
	-0.28	-0.26		-0.92	-0.92		-0.40	-0.39
0.296	0.44	0.43	0.889	-0.59	-0.60	2.30	-0.52	-0.53
	-0.18	-0.10		0.96	0.96		0.72	0.73
	-0.28	-0.33		-0.72	-0.71		-0.52	-0.53
	-0.79	-0.80		-0.09	-0.08		0.72	0.72
	0.0	0.0		0.0	0.0		-0.97	-0.99
	0.56	0.51		0.37	0.37		0.84	0.83

^a $\gamma(1,2) = \sum_k x_k(1)x_k(2)\frac{1}{\sqrt{2}}$ where x_k denotes a 1s atomic orbital of hydrogen and the summation is over all atoms in the cubic lattice, 4 layers of atoms, 9 atoms per layer.

^bCoefficients and virtual orbitals not listed are in similar agreement with the values shown.

Appendix II

Chemisorption: A Localization Transformation Definition of a Surface Region.

(Excerpts from a draft of a paper to be submitted for publication; taken from the Ph.D. Thesis of Tapani Pakkanen).

I. The Localization Transformation

Concerning adsorbate-surface interactions, although the chemisorption process cannot be regarded as a strictly local phenomenon, it is desirable to describe its essential features in terms of the interactions between the adsorbate and a limited region of the surface. This can be accomplished by an orbital localization procedure and by a subsequent limited variational treatment of the chemisorption site. The final description of the chemisorption process is obtained in an approximate field of the lattice, in contrast to small cluster studies where the external lattice interactions are neglected.

The orbital localization transformation is based on the maximization of electron exchange interactions with designated atoms on the surface. In this construction, two independent basis sets are involved, the first defines the orbitals which are to be transformed, $\{\phi_k\}$, and the second provides a representation of the system with which exchange interactions are to occur, $\{x_k\}$, i.e. the atomic orbitals of the designated atoms in the present application.

Consider a system described by a single determinant wavefunction

$$\psi = A(\phi_1, \phi_2, \dots, \phi_N)$$

where there are N_α and N_β spin orbitals $\{\phi_k\}$. Suppose this system is to interact with a second system described by orbitals $\{x_k\}$, $k = 1, 2, \dots, M$, where the second system can be thought of as a separate entity or as a part of the first system. The set $\{\phi_i\}$ is now transformed to linearly independent orbitals $\{\phi'_i\}$ which individually interact strongly with orbitals of the second system. To accomplish this the sum of exchange integrals γ is maximized.

$$\gamma = \sum_{k=1}^M [x_k(1)\phi(1) | \frac{1}{r_{12}} | x_k(2)\phi(2)] \geq 0$$

where $\phi = \sum_i c_i \phi_i$, (normalized), and the α and β spin orbitals are considered separately. This leads to an eigenvalue problem with solutions, ordered in eigenvalues $\gamma_1 \geq \gamma_2 \geq \dots \gamma_N$.

$$\gamma_1 \quad \phi'_1 = \sum_i c_{i1} \phi_i$$

$$\gamma_2 \quad \phi'_2$$

$$\vdots$$

$$\gamma_p \quad \phi'_p$$

$$\vdots$$

$$\gamma_N \quad \phi'_N = \sum_i c_{iN} \phi_i$$

The total wavefunction $\psi = A(\phi'_1, \phi'_2, \dots, \phi'_N)$ is identical to the initial wavefunction, and it is supposed that after some point γ_p in the eigenvalue spectrum, the orbitals $\phi'_{p+1} \dots \phi'_N$ exhibit negligible exchange interaction with representative orbitals $\{x_k\}$. On application to the transition metal lattice, delocalized molecular orbitals $\{\phi_i\}$

are available from the initial lattice description. The orbitals are $\{x_k\}$ free atom orbitals on atoms at the chemisorption site and serve as a representation of the valence part of the system which is most directly affected by subsequent interaction with the adsorbate.

The orbitals ϕ_i^l can be described qualitatively as representing either atomic orbitals or bonds in the solid. For a small number of designated surface atoms only a small number of orbitals ϕ_i^l can occur with large eigenvalues γ_i . The required orthogonality of the final set $\{\phi_i^l\}$ effectively rules out a concentration of more than a very limited number of orbitals in the region of space in which significant exchange with the local set $\{x_k\}$ would be possible; thus a suitable cut off value γ_p will exist. Given the above transformation, the orbital basis for the CI expansion is defined explicitly as follows:

The basis $\{f_i\}$ denotes normalized orbitals after orthogonalization, including a prior Gram-Schmidt orthogonalization of the $\{s_i\}$ to the interior orbitals.

A chemisorption study using localized site orbitals has several advantages to conventional cluster-adsorbate calculations. As pointed out earlier a relatively simple basis can be used to obtain an approximate description of the delocalized molecular orbitals of the initial cluster. After the localization transformation the adsorption site orbitals $\phi_1^l \dots \phi_p^l$ can be augmented with additional basis functions to assure an adequate description of the bond making and bond breaking processes. The adsorbate orbitals are also introduced at this step. The introduction of the additional basis functions to the initial calculations could lead to artificial polarization effects. This difficulty is avoided in the localized orbital treatment where the basis set improvement is restricted only to the region of space, where the limited variational calculation is performed. The lattice orbitals outside the localized set are kept fixed.

The localization does not exclude the possibility of delocalized bonding at the adsorption site. The delocalization of the electronic structure of the lattice can be probed by the γ -expansion method (Appendix I.), and once the range of multicenter bonding is established the size of the local site can be defined. Since the d-electrons are much more localized than the s-electrons in the transition metal lattice, the size of the local site can be different for s- and d-electrons.

II. Results on Linear Chains

$$\text{Ti}_n \ (n = 3, \dots, 10)$$

Figure II.1 shows the valence orbital energies of the Ti_n chains. The electronic structure of the chains $\text{Ti}_3, \dots, \text{Ti}_8$ is quite similar at the SUHF level. Every metal atom has two unpaired d electrons which are fully localized. The d-"band" of the chains have two additional electrons since the highest antibonding s molecular orbital is energetically unfavorable with respect to the empty d-levels. In the unrestricted calculations, all of the d-electrons are found to be unpaired, on the other hand the s molecular orbitals are essentially doubly occupied since the spatial parts of the α and β components are very similar. In Ti_9 and Ti_{10} also the second highest antibonding s level becomes less stable with respect to the d levels and subsequently the $4s \rightarrow 3d$ transfer is four electrons. Table II.1 shows the Mulliken populations of the chains. The average d occupation per atom approaches 2.4 in the longer chains.

The occupancy trend is in accordance with the band theory picture of Ti metal. A narrow d-band overlaps with a broad s-band which is not fully occupied. Bonding can be attributed to the vacant antibonding s molecular orbitals causing the occupied s electrons to be delocalized and bonding. The d-electrons are localized to atoms and do not engage in bonding.

Due to the limitations of the minimum basis set, the chains

Figure II.1. The eigenvalue spectrum of linear Ti chains. Connected levels are α and β s-type orbitals, other levels are d-type α orbitals.

Table II.1. Mulliken population analysis of Ti_n chains. Only one half of each chain is shown, since the other half is identical by symmetry. The populations of $2 d_{\pi}$ electrons per atom are included in the totals.

Chain	Orbitals	Atom 1	Atom 2	Atom 3	Atom 4	Atom 5
Ti_4	s_{α}	0.877	0.669			
	s_{β}	0.886	0.613			
	$d_{\sigma\alpha}$	0.168	0.787			
	Total	3.931	4.069			
Ti_5	s_{α}	0.915	0.733	0.705		
	s_{β}	0.926	0.717	0.715		
	$d_{\sigma\alpha}$	0.102	0.792	0.218		
	Total	3.940	4.241	3.640		
Ti_6	s_{α}	0.937	0.821	0.714		
	s_{β}	0.549	0.824	0.714		
	$d_{\sigma\alpha}$	0.043	0.524	0.466		
	Total	3.929	4.175	3.895		
Ti_7	s_{α}	0.950	0.882	0.738	0.758	
	s_{β}	0.962	0.895	0.743	0.760	
	$d_{\sigma\alpha}$	0.029	0.259	0.672	0.218	
	Total	3.942	4.037	4.154	3.735	
Ti_8	s_{α}	0.946	0.888	0.799	0.759	
	s_{β}	0.968	0.916	0.824	0.756	
	$d_{\sigma\alpha}$	0.031	0.241	0.427	0.444	
	Total	3.946	4.046	4.050	3.959	
Ti_9	s_{α}	0.947	0.848	0.790	0.807	0.707
	s_{β}	0.925	0.789	0.614	0.804	0.798
	$d_{\sigma\alpha}$	0.026	0.529	0.668	0.159	0.759
	Total	3.899	4.125	4.073	3.771	4.264
Ti_{10}	s_{α}	0.922	0.754	0.733	0.717	0.848
	s_{β}	0.936	0.757	0.745	0.701	0.849
	$d_{\sigma\alpha}$	0.074	0.766	0.223	0.738	0.235
	Total	3.933	4.278	3.700	4.156	3.932

are not energetically bound with respect to the metal atoms. The principal deficiency is the inflexible d-function which cannot expand, when the chain atom d-occupancy increases. This is seen clearly in the eigenvalue spectrum in which the d-orbital energy is directly proportional to the d-occupancy of the Ti center. An additional long range d-function would make the d-band much narrower.

The presence of unpaired electrons in the chains leads to a very large number of possible electronic states near the ground state. In order to avoid computational difficulties, e.g., the convergence of SCF procedures, and to maintain the maximum flexibility in the system, the d electrons were kept in the α -spin set. This requires that Hund's rule is obeyed on every Ti center. On the other hand the high net spin of the system is not very important, a state in which the neighboring Ti atoms have different spins is very close in energy. These conclusions are based on the fact that the intraatomic d-d interactions are much more stronger than the interatomic d-d interactions. Two of the d electrons in every atom were on d_{π} orbitals and the additional d-electrons were in the d_{σ} orbitals. Due to the d_{σ} -4s mixing this configuration provides a flexible adjustment mechanism for the d-s occupancy balance.

The Mulliken populations in Table II.1 show that the d-occupancy is very close to 2 on the end atoms of the chains, the additional d-electrons preferring the sites in the interior. The apparent localization of these electrons to every other Ti atom is

not very significant since there are other low lying states where the distribution of the d-electrons is different.

In the presence of several low lying states it is possible that the SCF procedure does not converge to the lowest state. Therefore a CI calculation was performed on Ti_5 . The d_{π} electrons were kept in the core and the variably occupied molecular orbitals consisted of five 4s molecular orbitals and of five $3d_g$ atomic orbitals which were symmetrical for convenience. The d_g orbitals are orthogonal to the s orbitals and approximately mutually orthogonal (the largest overlap = .004). The notation and the results of the CI calculations are shown in Table II.2. The initial single configuration state $|a\bar{b}|$ was obtained from a SUHF calculation. All single excitations from this state were generated and the six lowest states of the diagonalized CI matrix were passed to the final calculation. All single excitations and most double excitations (threshold⁴² = .00005) from the six reference states were included in the virtually complete CI calculation.

The results show that the lowest state is one where the two d-electrons are localized on atoms 2 and 4. The two next lowest states have one d-electron localized to the central Ti atom and the other is spread over the centers 2 and 4. Considering the uncertainties in the calculations, these three states are practically degenerate, but it is interesting to note that the lowest states found by the SUHF and CI methods have identical d-distributions. The fourth and fifth lowest

Table II.2. Configuration interaction results for Ti_5 linear.

Atomic d_g orbitals.

Center	1	2	3	4	5
d_g orbital	d_1	d_2	d_3	d_4	d_5

Symmetrized d_g orbitals

$$a = d_2 + d_4$$

$$b = d_3$$

$$c = d_2 - d_4$$

$$d = d_1 + d_5$$

$$e = d_1 - d_5$$

Notation: Configurations $A|\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3\bar{\phi}_3\phi_4\bar{\phi}_4xy| = |xy|$

ϕ_1, ϕ_2, ϕ_3 and ϕ_4 are s molecular orbitals.

State	Energy(eV)	Major configurations
1	0.0	$ a\bar{c} $
2	0.21	$ a\bar{b} $
3	0.24	$0.43 a\bar{c} + 0.85 c\bar{b} $
4	1.20	$ d\bar{b} $
5	1.20	$ e\bar{b} $

states correspond to excess d-occupations on the end atoms and are significantly higher in energy (1.2 eV). The same effect was also found in the SUHF studies where the d populations of the end atoms were close to 2.0.

The electronic structure of Ti chains suggests that the s and d orbitals have very different roles. The s orbitals are delocalized forming a partially filled band and this accounts for the conductivity properties of the metal. The d-electrons on the other hand are very localized and atom-like. The d occupation of the interior atoms of the solid is fractional as a result of a combination of numerous configurations corresponding to different d-localizations.

The most important feature is the energy balance between the s and d bands which determines the binding energy and possibly the reactivity at a given site.

III. Localization Studies on Ti Chains

The Ti chain wave functions were used to study the localization ideas for modeling extended lattice interactions. The exchange maximization procedure of Sec. I. was applied to two cases. The localizations to the end atom and to the two end atoms were considered as a function of the chain length. Since no transformation is needed to localize the d-orbitals, they were not considered. Figure II.2 shows the dependence of the maximization eigenvalue of the localized molecular orbitals as a function of the chain length. The end atom

Figure II.2. Exchange eigenvalues γ of the localized orbitals as a function of the chain length.

a) end atom localization

b) two end atom localization

localization produced in all cases one α and β orbital localized at the end atom. The eigenvalue γ does not depend on the chain length and is 0.37 a.u. The second most localized orbital has an eigenvalue of 0.01, the other eigenvalues being much smaller. The two end atom localization yields two localized s orbitals, one of which is localized to the end atom and another is localized on the second and third atom. These two orbitals have again large exchange eigenvalues (Figure II.2b) and the other eigenvalues are generally less than 0.01.

The Mulliken populations of the most localized orbitals of the two localization cases are shown in Table II.3. It is noteworthy that the end atom localized orbital has very small populations beyond the second atom and similarly the two end atom localized orbitals have small populations beyond the third atom. The result indicates that the tails of the orthogonal localized orbitals do not extend very far and their interactions should not be difficult to approximate.

The localization criteria based on the exchange eigenvalue seems to work very well: there is a distinctive break in the eigenvalue spectrum separating the site localized orbitals from the remaining orbitals.

Table II.3. Mulliken populations of the localized Ti_5 s orbitals.

a) End atom localization (one orbital)

b) Two end atom localization (two orbitals)

Center	1	2	3	4	5
Population a	0.932	0.051	0.001	0.008	0.002
Population b	0.920	0.735	0.272	0.048	0.024

0.1

0.0

b) Localized

Appendix III

The Definition of a Pseudoatom

Consider the chain of N bonded atoms,

(n electrons and m basis functions per atom) and the problem of describing a subsequent interaction with a molecule approaching atom (1) from the left. For this problem, we are primarily interested in the orbitals and the coulombic and exchange potential in the spatial region near the left end of the chain. Suppose that a complete calculation (unrestricted Hartree-Fock), including all electrons and basis functions, is available for the N atom chain. If the interest is in the simulation of an infinite chain, further assume that N has been chosen sufficiently large. We wish to consider replacing atoms M+1...N by an effective potential, V_{M+1} , such that the calculation on the M atom, V_{M+1} system provides an adequate representation of the N atom chain as far as interactions with the incoming molecule are concerned. Since the new system,

contains a different number of electrons and basis functions than the N atom chain, a direct comparison of the SCF solutions does not lead to a definitive conclusion. We proceed, instead, to compare the solutions at a localized orbital level, and take as the definition of a pseudoatom that potential which gives satisfactory agreement of the orbitals localized near the left end of the chain. Thus, the pseudoatom V_{M+1} is not designed to represent only a single atom, but instead is to simulate the effect of the remainder of the chain.

The method of localization is based on exchange maximization as described in Section IIIC. For a set of atomic orbitals $\{X_k\}$ on atom (1), the exchange integral sum

$$\gamma = \sum_k \langle \phi(1) X_k(1) | \frac{1}{r_{12}} | \phi(2) X_k(2) \rangle$$

is maximized to define localized orbitals ϕ expressed as a linear combination of the occupied orbitals of the SCF solution. For the N atom system, this results in a set of localized orbitals, ordered, $\phi_1 \phi_2 \dots \phi_p \dots \phi_{nN}$ corresponding to exchange eigenvalues $\gamma_1 \geq \gamma_2 \dots \geq \gamma_p \dots \gamma_{nN}$; similarly, assume that the M atom, V_{M+1} system gives localized orbitals

$$\phi'_1 \phi'_2 \dots \phi'_p \dots \phi'_{nM} \quad \text{and} \quad \gamma'_1 \geq \gamma'_2 \geq \dots \geq \gamma'_p \geq \dots \gamma'_{nM}$$

As noted in Section IIIC, only a small number of orbitals can exist with large exchange interaction and we suppose that these are p in number. The object is to choose V_{M+1} such that the two sets of localized orbitals are in satisfactory agreement through the first p members which correspond to orbitals with significant exchange interaction with atom (1), and indirectly with an electron system near atom (1).

Two simple forms of the potential V_{M+1} are to be considered:

$$(1) \quad V_{M+1}^0 = \frac{\lambda}{r_1} + \lambda' \int_{M+1}^{(2)} \frac{1}{r_{12}} dv_2$$

where ρ_{M+1} is the electron density of the free atom M+1, r_1 is a radial coordinate with origin at atom M+1, and λ and λ' are variable parameters.

$$(2) \quad V_{M+1} = V_{M+1}^0 + \sum_m \gamma_m |X_m\rangle \langle X_m|$$

where X_m is an atomic orbital of atom M+1 and the γ_m are variable

parameters. Identical parameters will be assumed for equivalent d orbitals to give two variables γ_s and γ_d in the application to a chain of Ti atoms. A choice of potential leads to a set of localized orbitals which are to be compared with those of the N atom chain by evaluation of the orbital overlap.

By the same procedure, a more flexible definition of a pseudoatom, M+1, is possible in which selected basis functions of the atom M+1 are allowed to contribute explicitly to the M atom, V_{M+1} system. For example, in the present Ti application it would be of interest to include the 4s orbital of atom M+1 and to have the pseudoatom represent the effect of the 3d orbitals of atom M+1 and the remainder of the chain.

The above argument, it is noted, is qualitatively similar to the idea of reproducing the local density of states on the left-most atoms by means of a M atom chain plus potential V_{M+1} .