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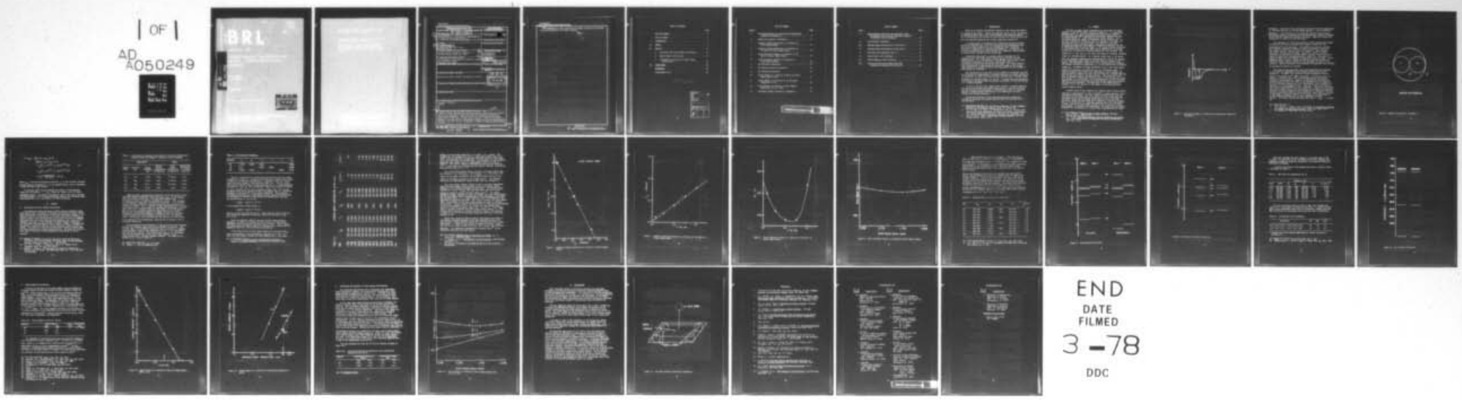

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ALPHA

A method has been developed for performing accurate total energy calculations using the X-alpha theory without the usual arbitrariness in selection of calculational parameters. The use of relatively high ℓ-values and atomic sphere radii in the ratio of their atomic (covalent) radii led to results in agreement with experiment for dissociation energies and equilibrium separation distances in NO, CO, and SN. In addition, a method of obtaining dipole moments is given.

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The importance of these quantities in a model of erosion is discussed along with suggestions for further research.

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I. INTRODUCTION

There is at present considerable interest in the causes and effects of erosion of gun tubes[1]. Recent experimental results on the interaction of combustion gases with steel alloys indicate that chemical effects can be important in the erosion of steel and may even exceed those of the melt and wipe-off mechanism for certain combustion conditions[2].

A reliable means of computationally simulating erosion processes would be a valuable tool to aid in interpreting the experimental data and in providing estimates for erosion behavior under conditions difficult or impossible to simulate experimentally. In addition, an accurate microscopic model would advance our fundamental understanding of hot gas-metal surface reaction mechanisms.

A detailed microscopic or quantum-chemical treatment of the interaction of a gas with a metal surface may be divided into two separate areas: 1) a description of the movement of the atoms during collisions in response to the forces exerted upon them; 2) a description of the forces acting upon the atoms. This latter description is equivalent to specifying the potential energy of the system since the force is always derivable from a potential for any system in which energy is conserved.

The interaction of a gas with a metal surface is intimately involved in the process of chemisorption, a process which may be loosely defined as the adsorption of atoms or molecules upon a surface with a binding energy in excess of a certain energy, say one eV.[3] In many cases the adsorption energies are high enough that the process corresponds to electron sharing, i.e., chemical bonding.

In view of the fact that computational methods of quantum chemistry are having increasingly far ranging applications, a task was initiated with the objective of determining if these methods might be profitably applied to understanding chemisorption, thus enabling one to gain insight into erosion processes.

During the execution of this task much previously unreported information regarding the quantum-chemical model was obtained and is reported here.

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[1] Tri-Service Gun Tube Wear and Erosion Symposium, US Army Armament Research and Development Command, Dover, NJ, March 1977.

[2] A.C. Alkidas, L.H. Caveny, M. Summerfield, and J.W. Johnson, High Pressure and High Temperature Gas Metal Interactions, presented at 13th JANNAF Combustion Conference, Monterey, CA, September, 1976.

[3] S.K. Lyo and R. Gomer, Interactions on Metal Surfaces, Springer-Verlag, Berlin, 1975, p. 41.

II. THEORY

In order to supply useful information on the process of chemisorption, a theoretical model should be capable of: 1) describing excited states, 2) predicting reasonable dissociation energies, 3) predicting reasonable equilibrium internuclear separations; and, for some problems, 4) predicting accurate dipole moments. Also, the method should be capable of reasonably priced calculations. An accurate description of excited states is necessary since many of the atoms will be in excited states. The need for an accurate dissociation energy and equilibrium internuclear separation can best be understood with the aid of Figure I. Two atoms, forming a molecule in its ground state, will have their nuclei separated by an average distance r_o, at which the electronic energy will be a minimum. Any separation, r, less than r_o will cause the energy to increase, becoming larger as r becomes smaller. As r becomes larger than r_o the energy will also increase, asymptotically approaching the sum of the energies of the individual atoms, shown as the zero value of energy in the figure. The difference between this zero of energy and the energy at the average internuclear separation, r_o, is the dissociation or bonding energy, E_b. An amount of energy equivalent to E_b is the least amount required to dissociate the molecule into its constituent atoms. A similar situation occurs when a gas approaches a metal surface; the total electronic energy will vary, the occurrence of a minimum implying that the gas may stick to the metal surface. One would like to be able to calculate whether the gas does stick to the surface and, if so, how strongly it is held there. The characterization of these problems requires an accurate determination of equilibrium separation distances and dissociation energies. The importance of the dipole moment is thought to be in its relation to the change of work function with crystal symmetry plane[4].

A method which we have explored for studying these various aspects relating to chemisorption is the X-α method[5], a single-electron, self-consistent-field method. The term "single-electron" means that the electrons are each considered to be moving in a field resulting from the atomic nuclei and an average charge density due to all other electrons, except the particular one in question, considered together. This is in distinction to a many-body approach where the interaction of each electron with each other electron would be explicitly taken into account. To achieve self-consistency, one starts with an initial potential for the molecule, V, in this case a superposition of atomic

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4. L.D. Schmidt, in <u>Interactions on Metal Surfaces</u>, Springer-Verlag, Berlin, 1975, p. 41.
5. J.C. Slater, <u>The Self-Consistent Field for Molecules and Solids</u>, Vol. 4 of Quantum Theory of Molecules and Solids, McGraw-Hill, (New York), 1974.

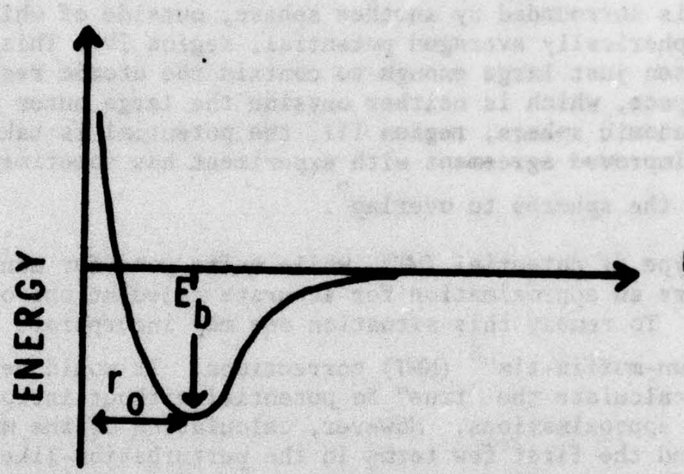

Figure 1. Electronic Energy as a Function of Internuclear Separation (schematic).

potentials. From this initial potential the single-electron eigenvalues, ϵ_i, the wave function, ψ, and the charge density, ρ, are successively generated. A new potential may be generated from the charge density. The entire process is iterated until the new potential differs insignificantly from the immediately previous potential. When this occurs, the calculation is said to be self-consistent.

For a molecule or solid the Xα theory is often implemented through the multiple-scattering formalism which adopts a muffin-tin (MT) approximation[6] to the potential. This muffin-tin potential consists of a separate spherically symmetric region of potential centered at each atomic nucleus, regions I and II in Figure 2. These regions are usually chosen to be touching. The entire cluster of atomic potentials is surrounded by another sphere, outside of which is also a region of spherically averaged potential, region IV. This sphere is usually chosen just large enough to contain the atomic regions. In the remaining space, which is neither outside the large outer sphere or inside any atomic sphere, region III, the potential is taken to be a constant. Improved agreement with experiment has sometimes been obtained by allowing the spheres to overlap[7].

This type of potential (MT), while quite good for many purposes, is too severe an approximation for accurate calculations of many properties. To remedy this situation one may incorporate what are known as "non-muffin-tin"[8] (NMT) corrections. It would be costly at present to calculate the "true" Xα potential without introducing restrictive approximations. However, calculation of the muffin-tin potential and the first few terms in the perturbation-like expansion for the difference between the "true" Xα potential and the muffin-tin potential is not exceedingly costly. Thus one is able to calculate a more accurate approximation to the Xα potential. These NMT corrections are able to remove many of the restrictions of the muffin-tin potential while not increasing computer-time requirements to impractical amounts. The NMT corrections consist of terms which are linear (NMT-L) in $\Delta\rho$ and a term which is quadratic (NMT-Q) in $\Delta\rho$ where $\Delta\rho$ is an approximation of the difference between the x-α and x-α muffin-tin charge density. The energy arising from these NMT terms, $< \Delta E_{x\alpha} >$, is given by

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[6] Ibid, pg. 101.

[7] K.H. Johnson, F. Herman, and R. Kjellander in, Electronic Structure of Polymers and Molecular Crystals, Plenum (New York), 1975.

[8] J.B. Danese, J. Chem. Phys. 61, 3071 (1974).

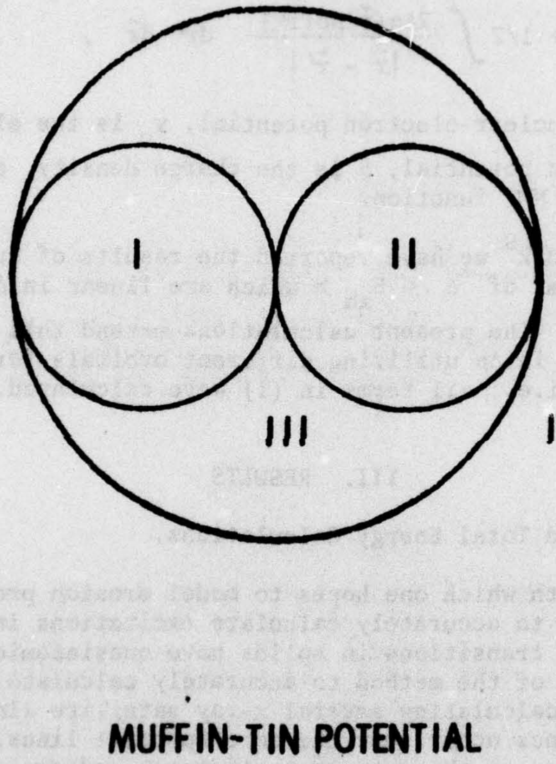

Figure 2. Muffin-tin-potential (schematic).

$$
\begin{aligned}
\Delta < E_{X\alpha} > = & \int \Delta\rho\,(\bar{r})\ \Delta v_{Ne}\,(\bar{r})\ d\bar{r} \\
& + \int \Delta\rho\,(\bar{r})\ \Delta v_{C}\,([\bar{\rho}],\bar{r})\ d\bar{r} \\
& + c_{\alpha} \int \left(\rho_{\uparrow}\,(\bar{r})^{4/3} - [\,\bar{\rho}_{\uparrow}(\bar{r})]^{4/3} \right) d\bar{r} \qquad (1) \\
& + c_{\alpha} \int \left(\rho_{\downarrow}(\bar{r})^{4/3} - [\,\bar{\rho}_{\downarrow}(\bar{r})]^{4/3} \right) d\bar{r} \\
& + 1/2 \int \frac{2\Delta\rho\,(\bar{r})\Delta\rho\,(\bar{r}')}{|\bar{r} - \bar{r}'|}\ d\bar{r}'\ d\bar{r}\ ,
\end{aligned}
$$

where v_{ne} is the nuclear-electron potential, v_C is the electron- electron Coulomb interaction potential, ρ is the charge density, and a Δ preceding a term indicates a NMT function.

In previous work[9] we have reported the results of calculations using only the terms of $\Delta < E_{X\alpha} >$ which are linear in $\Delta\rho$ in a spin-independent model. The present calculations extend this work to include the term quadratic in $\Delta\rho$ utilizing different orbitals for different spins (spin-polarized), i.e., all terms in (1) were calculated.

III. RESULTS

A. Excitation and Total Energy Calculations.

Any method with which one hopes to model erosion processes in gun tubes must be able to accurately calculate excitations in metals. Since many radiationless transitions in solids have quasiatomic aspects[10], we tested the ability of the method to accurately calculate excitations in metallic atoms by calculating several x-ray satellite lines in aluminum. These satellite lines occur near the core spectral lines, those of the innermost electrons, as the outermost electrons undergo transitions. The calculated and experimental results, shown in Table I, indicate that excitations in metallic atoms may be satisfactorily studied by the Xα method. The results are the more striking since multiply ionized atoms are being described by a single electron theory. The value of α used in each case is that which may be determined by satisfying the virial theorem[11].

---

9. Douglas A. Ringers, "Electronic Excitation in NO and SN by the Non-Muffin-Tin-X-Alpha Method", BRL Report 1968, US Army Ballistic Research Laboratory, March 1977. (AD #A037802)
10. L.I. Yin, I. Adler, T. Tsang, M.H. Chen, D.A. Ringers and B. Crasemann, Phys. Rev. A9, 1070 (1974).
11. Douglas A. Ringers, "Xα Calculation of Transition Energies in Multiply Ionized Atoms", BRL Memorandum Report No. 2766, June 1977. (AD #A043091)

Table I. Experimentally Observed X-Ray Satellite Lines and Theoretically Derived Transition Energies in Multiply Ionized Aluminum.

Experiment[12]			Theory		
Diagram Line	Satellite Line	Energy Difference (eV)	Initial Vacancy Configuration of Satellite	Final Vacancy Configuration of Satellite	Energy Shift With Respect To Diagram Lines (eV)
$K\alpha_2$	$K\alpha'$	5.69	1s2p	^3P 2p,2p	6.90
$K\alpha_2$	$K\alpha_4$	11.85	1s2p	^1D 2p,2p	12.00
$K\alpha_2$	$K\alpha_5$	19.71	1s2p	^1S 2p,2p	19.63
$K\alpha_2$	$K\alpha_6$	23.56	1s2p	2p,3s	23.15

Among the first test molecules studied by the Xα NMT method at the Ballistic Research Laboratory were nitric oxide (NO), carbon monoxide (CO), and sulfur nitride (SN). The open shell molecule NO has been the subject of numerous experimental studies. This compound is of fundamental importance in ballistics processes. It is a product of many gas-phase reactions involving propellants and explosives, is corrosive to metals, and is a product of many chemiluminescent reactions. Since additionally a great amount of experimental information is available on NO it is a desirable molecule upon which to test the method. Much of the same rationale applies to carbon monoxide, but from a theoretical or modelling viewpoint it differs in that all electronic occupied orbitals are fully occupied (closed shell) in the ground state. Studies were also performed upon the molecule SN, since $(SN)_x$ is an explosive[13], one-dimensional conductor and is similar to NO in electronic structure.

The calculations were performed in a spin-polarized mode (different orbitals for different spins) for the MT and NMT-L corrections. Due to their small size the NMT-Q corrections were calculated in a nonspin-polarized model. Partial wave expansions up to $\ell = 2$ ("d functions") were used on all centers. The α values were those of the corresponding atom (spin-polarized) in the case of open shells) in the atomic regions with a suitable average elsewhere. The computational parameters are listed in Table II.

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12. Ford, O.R., Phys. Rev. 41, 577 (1932).
13. Sharma, J., private communications.

Table II. Calculational Parameters.

Molecule	r_e	α_N	α_O	α_C	α_S	α_{IS}
NO	2.1758	.74725	.74118			.74422
CO	2.17		.74118	.75331		.74725
SN	2.8765	.74952			.72183	.73274

The test calculations on the NO molecule indicated that the linear non-muffin-tin terms, E_L, required little additional computer time beyond a muffin-tin calculation and amounted to 1 percent of the total calculated electronic energy of the molecules (Table III). This is on the order of the bonding energy for many molecules and so is indeed important. The quadratic term, E_Q, took considerably longer and accounted for about 0.1 to 0.2 percent of the total electronic energy (Table III) for NO, an amount which can be ignored for many, but perhaps not all, excitation processes as calculated by total energy differences. When studying excitation processes, one is interested in total energy differences and the difference in quadratic terms between the ground state (gs) and any excited state, i, is, for NO,

$$| E_Q(gs) - E_Q(i) | < .07 \text{ ryd} .$$

If we consider only valence states, v,

$$| E_Q(gs) - E_Q(v) | < .02 \text{ ryd} .$$

Similar results were observed for SN. These results indicate that for most excitations quadratic corrections will be on the order of one eV or less.

Since the quadratic (NMT-Q) term was the most computationally demanding, an effort to determine if there existed any predictable dependence upon calculational parameters was in order. Such a dependency would enable the NMT-Q terms to be estimated for a desired set of parameters from only a few well-chosen calculations.

In the study of NO the outer sphere radius was increased from a value corresponding to the experimental separation of 2.1758 a.u.[14], where the outer sphere touches the atomic spheres and is just large

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[14] G. Herzberg, Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, Van Nostrand, Princeton, 1950.

TABLE III. BINDING ENERGY CONTRIBUTIONS IN NO (RYD.)

ORB.	$-E_{MT}$	$-E_L$	E_Q	$-E_T$	I_P (CALC.)	I_P (EXP.)
$2\pi\uparrow$	255.1068	2.9811	.3380	257.7494	.74	.74
$1\pi\downarrow$	254.5623	2.9906	.3207	257.2322	1.28	
$1\pi\uparrow$	254.4838	2.9914		257.1545	1.35	
$5\sigma\downarrow$	254.8150	2.7154	.3236	257.2068	1.30	1.23
$5\sigma\uparrow$	254.7162	2.7276		257.1202	1.38	1.36
$4\sigma\downarrow$	254.2742	2.8572	.3220	256.8094	1.62	1.60
$4\sigma\uparrow$	254.3596	2.8533		256.8909	1.70	1.71
$3\sigma\downarrow$	253.4612	2.5941	.2870	255.7683	2.77	2.98
$3\sigma\uparrow$	253.3792	2.6148		255.7070	2.83	3.22
$2\sigma\downarrow$	225.7737	3.0397	.3418	228.4716	30.01	30.16
$2\sigma\uparrow$	225.6887	3.0302		228.3711	30.11	30.27
$1\sigma\downarrow$	216.1039	3.0618	.4136	218.7521	39.73	39.93
$1\sigma\uparrow$	216.0862	3.0736		218.7462	39.74	39.99
GND.	255.8908	2.9376	.3442	258.4842		

enough to enclose them completely, to a value .4 a.u. larger. The increase was in increments of .05 a.u. with atomic-sphere radii held fixed. The calculations included both the terms which are first order in $\Delta\rho$ and those which are second-order. The dependency of the quadratic term upon outer sphere radius is approximately linear as shown in Figure 3. The circles represent calculations where partial waves up to $\ell = 2$ were used on all centers and the squares represent calculations using partial waves up to $\ell = 3$.

For a fixed outer-sphere radius, the ratio of atomic-sphere radii was allowed to vary from $R_N/R_O = .86$ to $R_N/R_O = 1.17$, where R_N is the radius of the sphere centered on the nitrogen nucleus and R_O is the radius of the sphere centered on the oxygen nucleus. The quadratic correction was approximately linear in this case also (Figure 4).

The total energy, however, proved to have a nonlinear dependence upon both atomic-sphere radius (Figure 5) and outer-sphere radius (Figure 6) with a definite minimum in both cases. The minimum energy occurred at a value of R_N/R_O very near that which one would obtain using the respective values of Slater atomic radii[15]. The energy minimum is slight, amounting to only .15 rydberg less than that obtained for an outer-sphere radius corresponding to the experimental separation, and occurring about .2 a.u. larger than the value corresponding to the experimental separation distance. The values of atomic- and outer-sphere radii corresponding to the total energy minima were used in ensuing calculations. The outer-sphere radius for NO of 2.3758, which corresponded to the energy minimum, was 0.2 a.u. larger than the minimum radius required to enclose the atomic region, viz., 2.1758 a.u. This larger value is markedly different from the radius usually chosen, i.e., the minimum radius necessary to enclose the atomic regions, and resulted in improved results for dissociation energy and electronic excitation energies in NO.

Using these selected values of radii, calculations were made of the orbital ionization energies in NO. The ionization energies for each occupied, single-electron orbital were calculated as total energy differences. In Table III are listed the muffin-tin energy, linear NMT correction, quadratic NMT correction, total energy, and ionization potential. For comparison experimentally obtained values[16] of the ionization potentials are also listed.

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15. J.C. Slater, Quantum Theory of Molecules and Solids, Vol. 2, McGraw-Hill, New York, 1965.
16. K. Siegbahn, et al., ESCA Applied to Free Molecules, North-Holland Amsterdam, 1971.

* The ordinate is taken as six-tenths of the R_n to R_O ration for convenience.

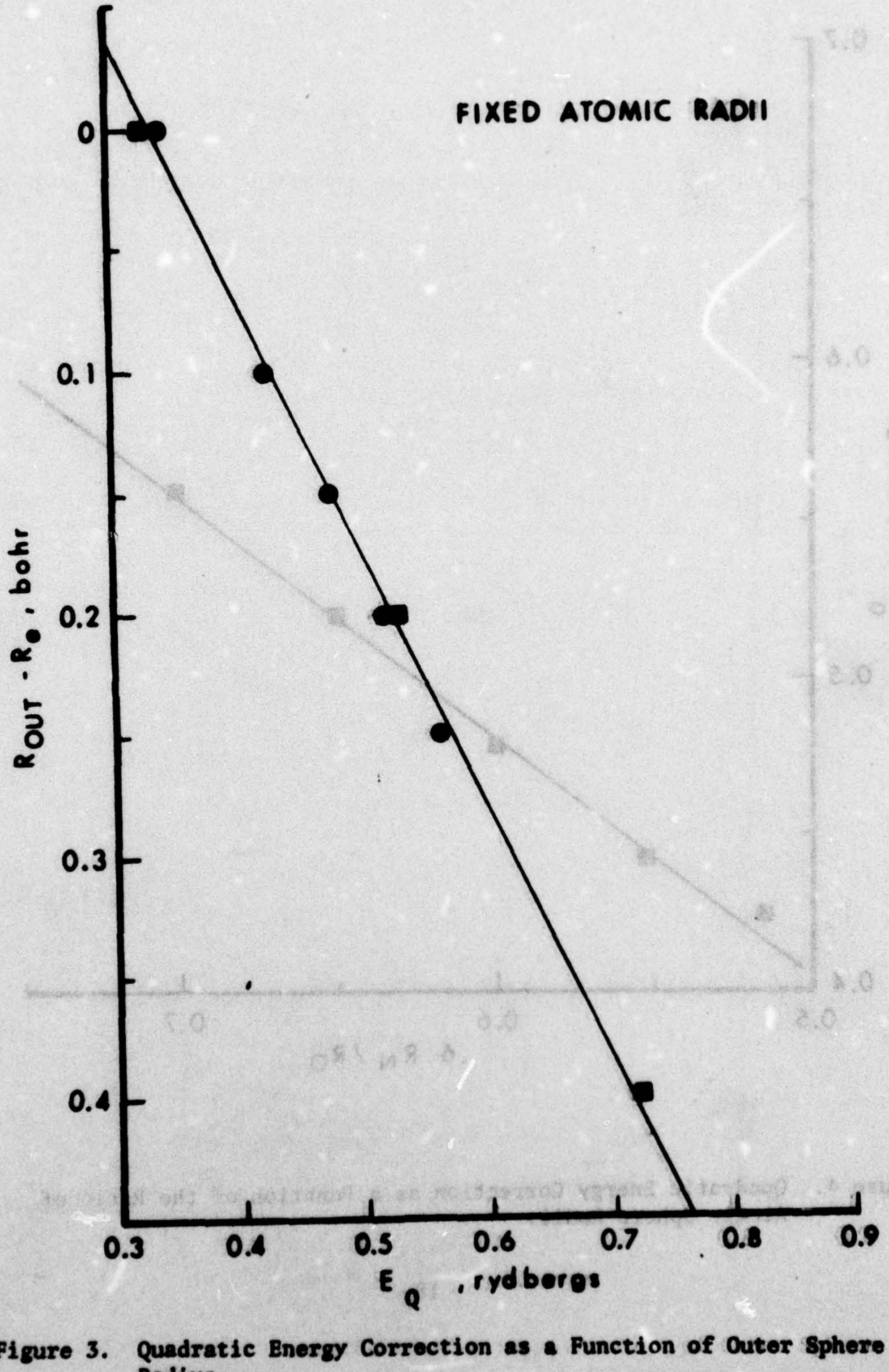

Figure 3. Quadratic Energy Correction as a Function of Outer Sphere Radius.

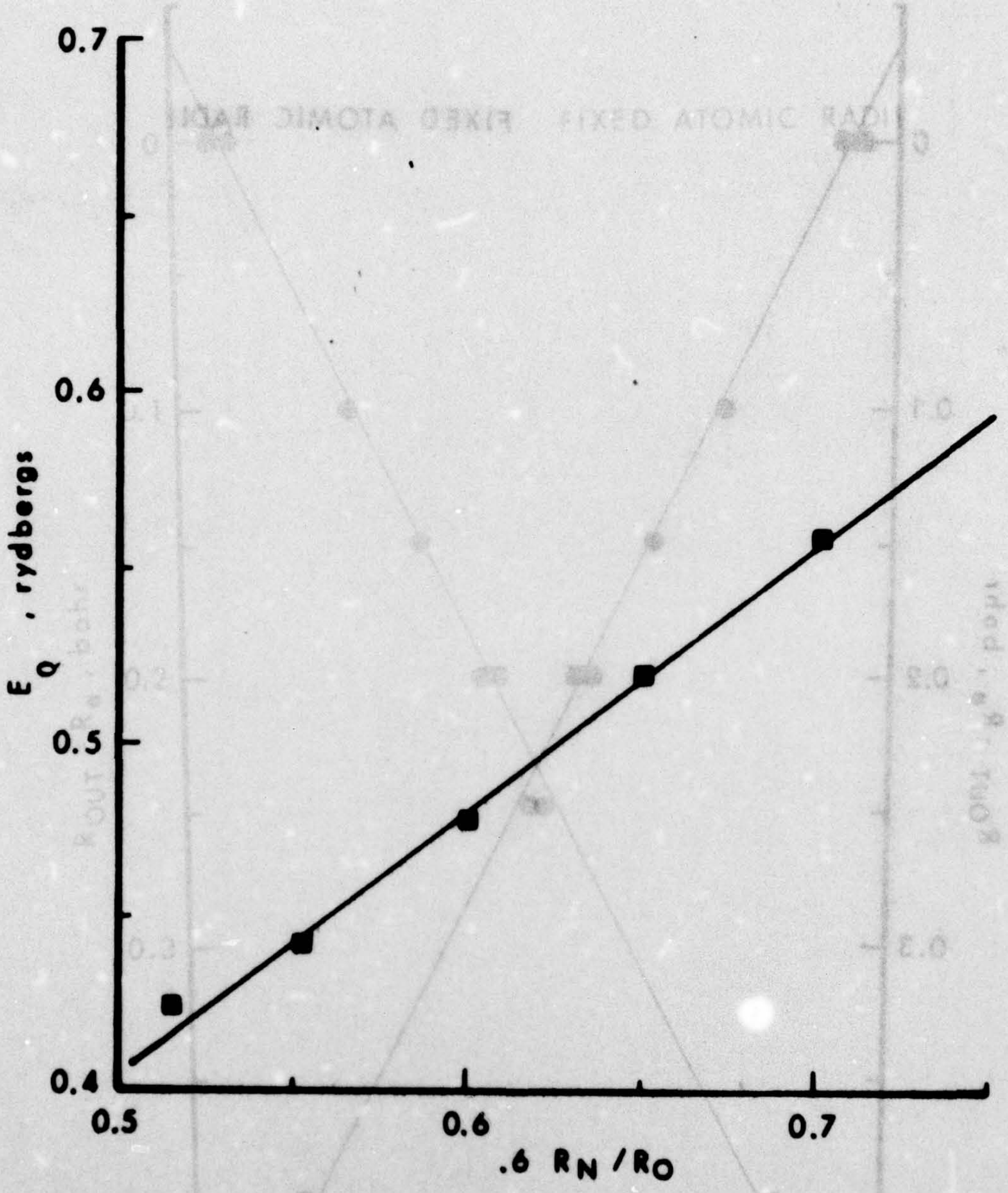

Figure 4. Quadratic Energy Correction as a Function of the Ratio of Atomic Sphere Radii.

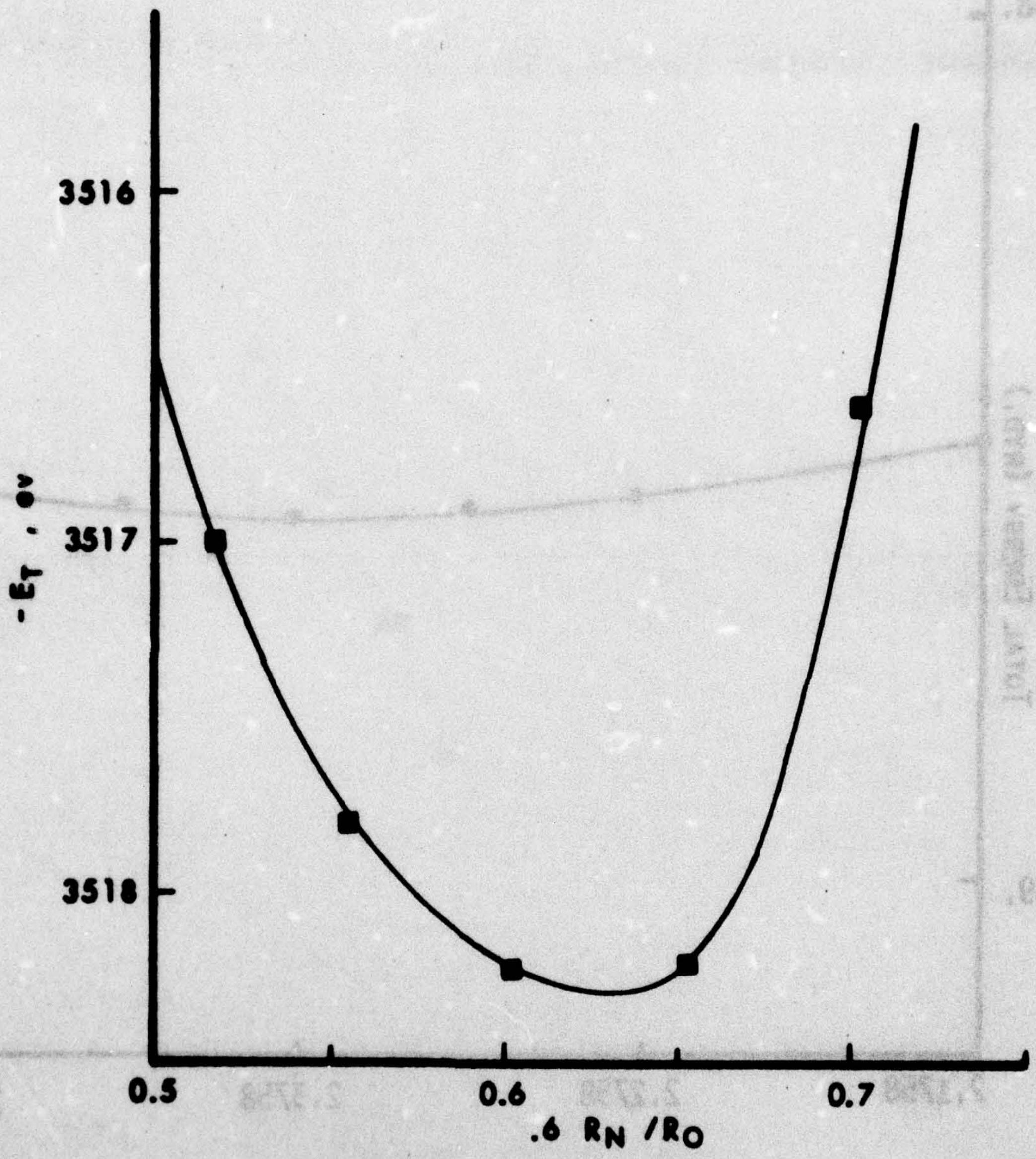

Figure 5. Total Electronic Energy as a Function of the Ratio of Atomic Sphere Radii.

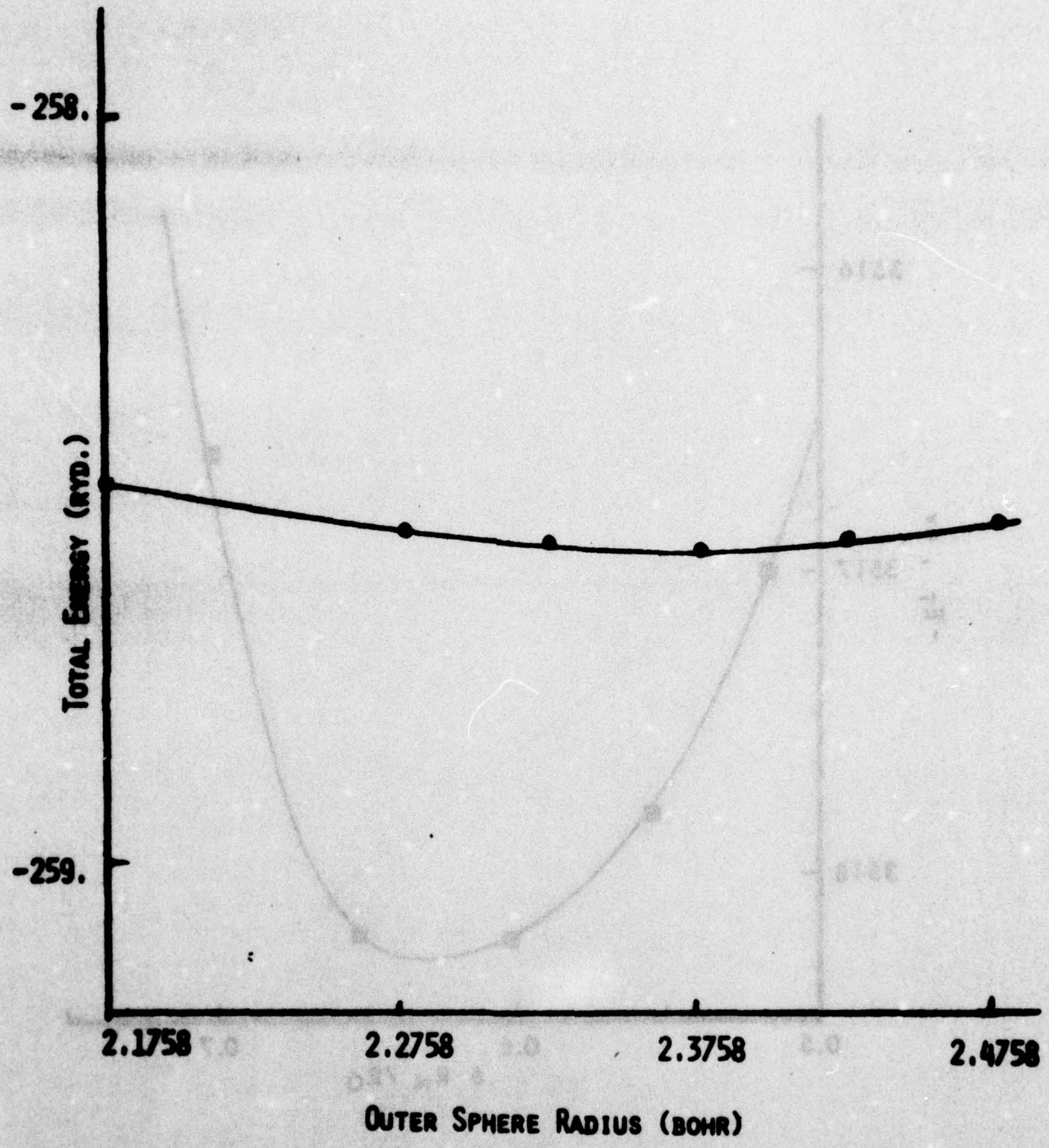

Figure 6. Total Electronic Energy as a Function of Outer Sphere Radius.

These results are plotted in Figure 7. Note that the 1 π level is above the 5 σ level of corresponding spin, in disagreement with reported overlapping-sphere calculations[17], but supported by other calculations[18]. In the muffin-tin calculation without NMT corrections these states are in the opposite order. For this simple system omission of the NMT terms yields results which are not even qualitatively correct.

Similar calculations of the ionization energies for each valence orbital were performed on SN with the results shown in Figure 8 and listed in Table 4. In SN a situation similar to that in NO occurs: the NMT corrections rearrange the ordering. This similarity in the ordering of the ionization levels reflects the similar ground state electronic structure of the two molecules. The ground state occupancy for NO is a core consisting of a closed shell (1 s shell) plus a valence configuration of $(3\sigma)^2\ (4\sigma)^2\ (5\sigma)^2\ (1\pi)^4\ (2\pi)^1$ while that of SN consists of a somewhat larger core of closed shells plus a valence configuration of $(5\sigma)^2\ (6\sigma)^2\ (7\sigma)^2\ (2\pi)^4\ (3\pi)^1$.

Table IV. Binding Energy Contributions in SN (ryd.)

ORB.	$-E_{MT}$	$-E_L$	E_Q	$-E_T$	I_p(calc.)
$3\pi\uparrow$	900.5439	2.8089	.4355	902.9173	.63
$2\pi\uparrow$	900.1338	2.8355	.4233	902.5460	1.00
$2\pi\downarrow$	900.1980	2.8409		902.6156	.93
$7\sigma\uparrow$	900.2938	2.5936	.4090	902.4784	1.07
$7\sigma\downarrow$	900.3719	2.5385		902.5014	1.04
$6\sigma\uparrow$	899.8342	2.7212	.4115	902.1439	1.40
$6\sigma\downarrow$	899.8998	2.7189		902.2072	1.34
$5\sigma\uparrow$	899.2885	2.5285	.3804	901.4366	2.11
$5\sigma\downarrow$	899.3562	2.5220		901.4978	2.05
Gnd.	901.2125	2.7791	.4461	903.5455	

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17. D.R. Salahub and R.P. Messmer, J. Chem. Phys. 64, 2039, 1976.
18. P.E. Cade, W.M. Huo and J.B. Greenshields, Atomic Data and Nuclear Data Tables, 15, 1, 1975.

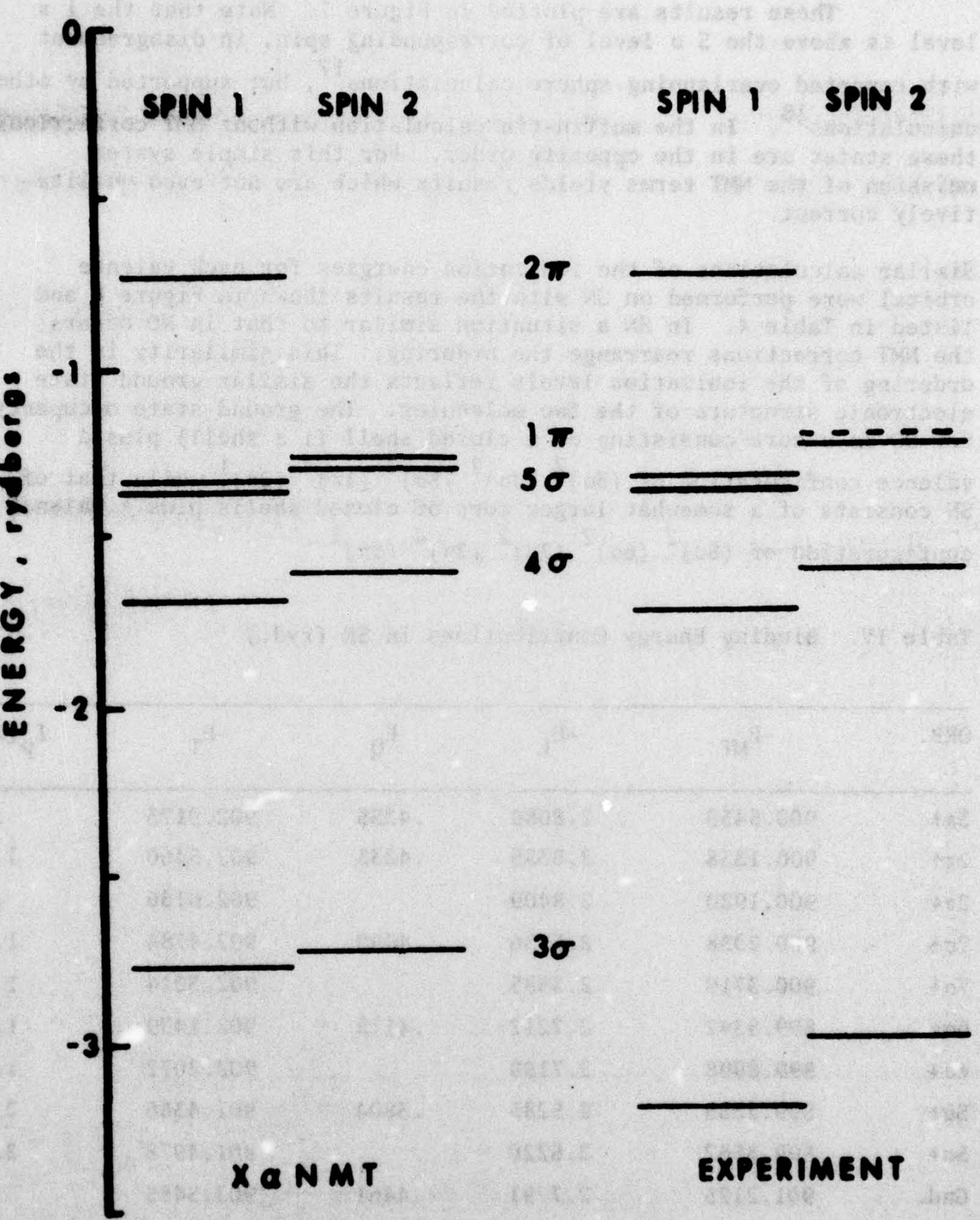

Figure 7. NO Ionization Potentials.

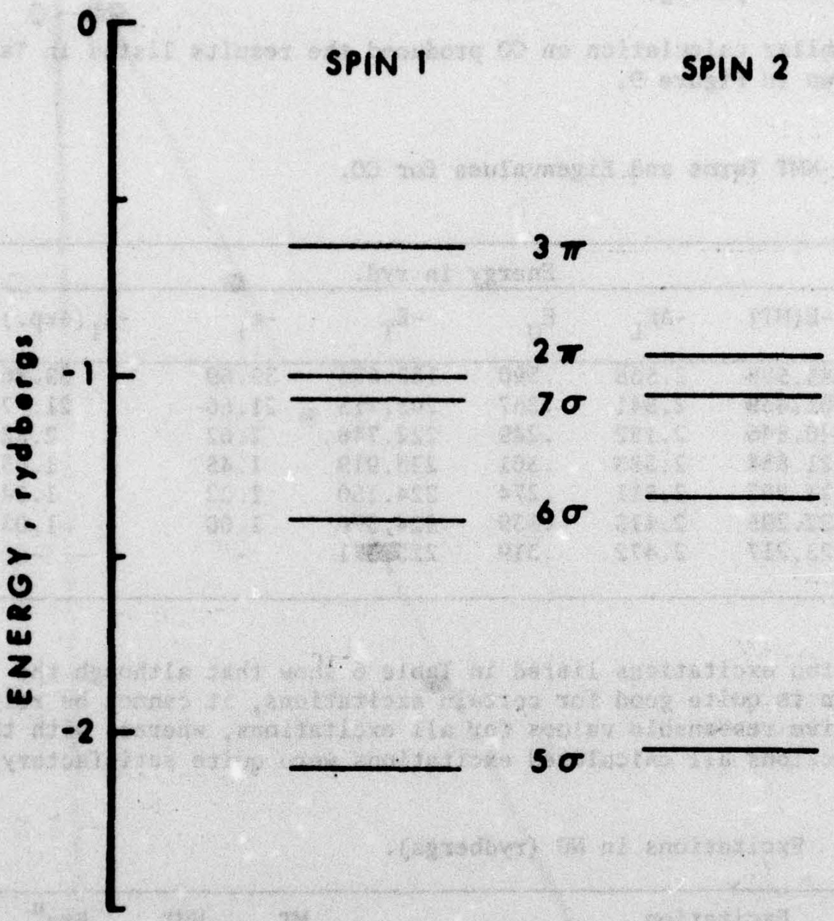

Figure 8. SN Valence Ionization Potentials.

Note that although the total energy in the ground state of SN is nearly 3.5 times that of NO, differing by over 600 rydbergs, the respective linear and quadratic non-muffin tin corrections differ by less than 0.2 rydberg.

A similar calculation on CO produced the results listed in Table V and shown in Figure 9.

Table V. NMT Terms and Eigenvalues for CO.

	Energy in ryd.					
State	$-E(MT)$	$-\Delta E_L$	E_Q	$-E_T$	$-\varepsilon_i$	$-\varepsilon_i(\text{exp.})$[19]
O 1s	183.508	2.568	.390	185.686	39.69	39.86
C 1s	201.439	2.541	.267	203.713	21.66	21.77
3 σ	220.846	2.152	.249	222.748	2.62	2.82
4 σ	221.838	2.383	.301	223,919	1.45	1.45
1 π	221.907	2.511	.274	224.150	1.22	1.24
5 σ	222.295	2.415	.339	224.370	1.00	1.03
G.S.	223.217	2.472	.319	225.371	-	-

The two excitations listed in Table 6 show that although the muffin-tin is quite good for certain excitations, it cannot be relied upon to give reasonable values for all excitations, whereas with the NMT corrections all calculated excitations were quite satisfactory.

Table VI. Excitations in NO (rydbergs).

Excitation	MT	NMT	Exp[a]
$(1\pi)^4\ (3\sigma)^2\ (2\pi)^1 \rightarrow (1\pi)^3\ (3\sigma)^2\ (2\pi)^2$	.56	.54	.53
$(1\pi)^4\ (3\sigma)^2\ (2\pi)^1 \rightarrow (1\pi)^4\ (3\sigma)^1\ (2\pi)^2$	.34	.65	.63

[a] Average over values deduced from empirical curves as given in reference 20.

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19. Bagus, P., et al., Solid State Comm. 20, 5, 1976.
20. LeFebure-Brion, H. and C.M. Moser, J. Chem. Phys. 44, 2951, 1966.

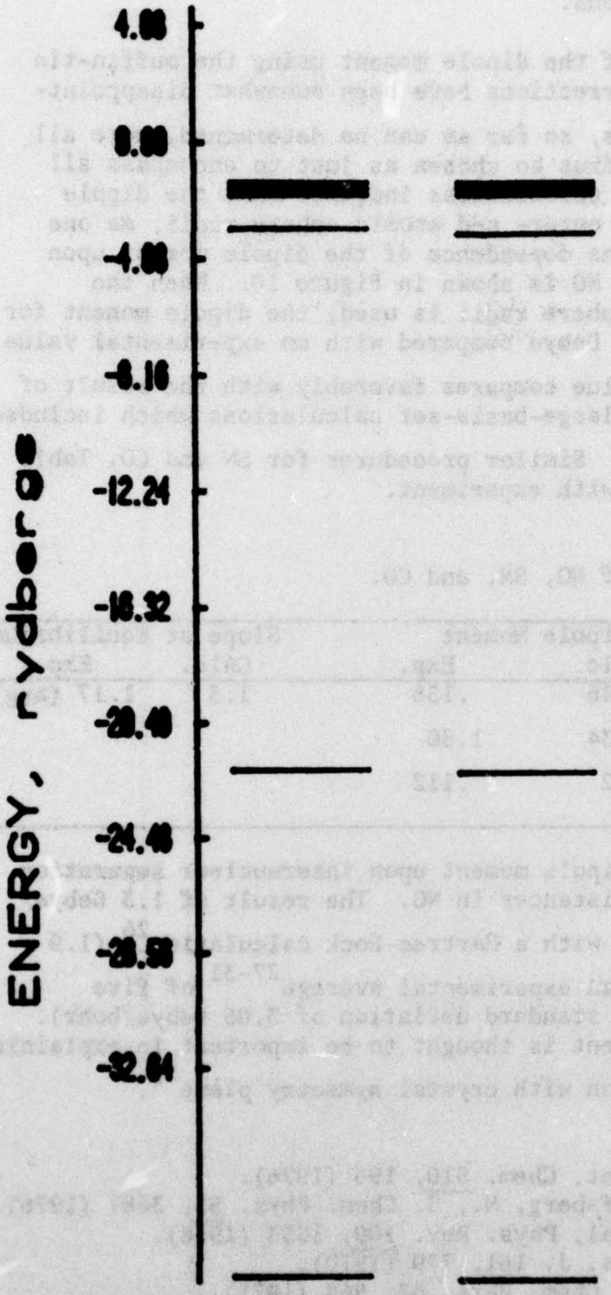

Figure 9. CO Ionization Potentials.

B. Dipole Moment Calculations.

Previous calculations of the dipole moment using the muffin-tin potential without the NMT corrections have been somewhat disappointing[21,22]. These calculations, so far as can be determined, were all done with an outer-sphere radius so chosen as just to encompass all atomic spheres. The present calculations indicate that the dipole moment depends strongly upon outer- and atomic-sphere radii, as one would intuitively expect. The dependence of the dipole moment upon the ratio of atomic radii in NO is shown in Figure 10. When the "energy selected" value of sphere radii is used, the dipole moment for NO was calculated to be .146 Debye compared with an experimental value of .157[23,24] Debye. This value compares favorably with the result of .147 Debye obtained in very-large-basis-set calculations which included configuration interaction[25]. Similar procedures for SN and CO, Table VII, also were in agreement with experiment.

Table VII. Dipole Moments of NO, SN, and CO.

Material	Dipole Moment		Slope at Equilibrium	
	Calc.	Exp.	Calc.	Exp.
NO	.146	.158	1.3	1.17 (avg)
SN	1.834	1.80		
CO	.12	.112		

The dependence of the dipole moment upon internuclear separation was calculated for several distances in NO. The result of 1.3 Debye/bohr, Figure 11, is compared with a Hartree-Fock calculation[26] (1.9 Debye/bohr) as well as with an experimental average[27-31] of five values (1.17 Debye/bohr with standard deviation of 3.05 Debye/bohr). The effect of the dipole moment is thought to be important in explaining the variation in work function with crystal symmetry plane[32].

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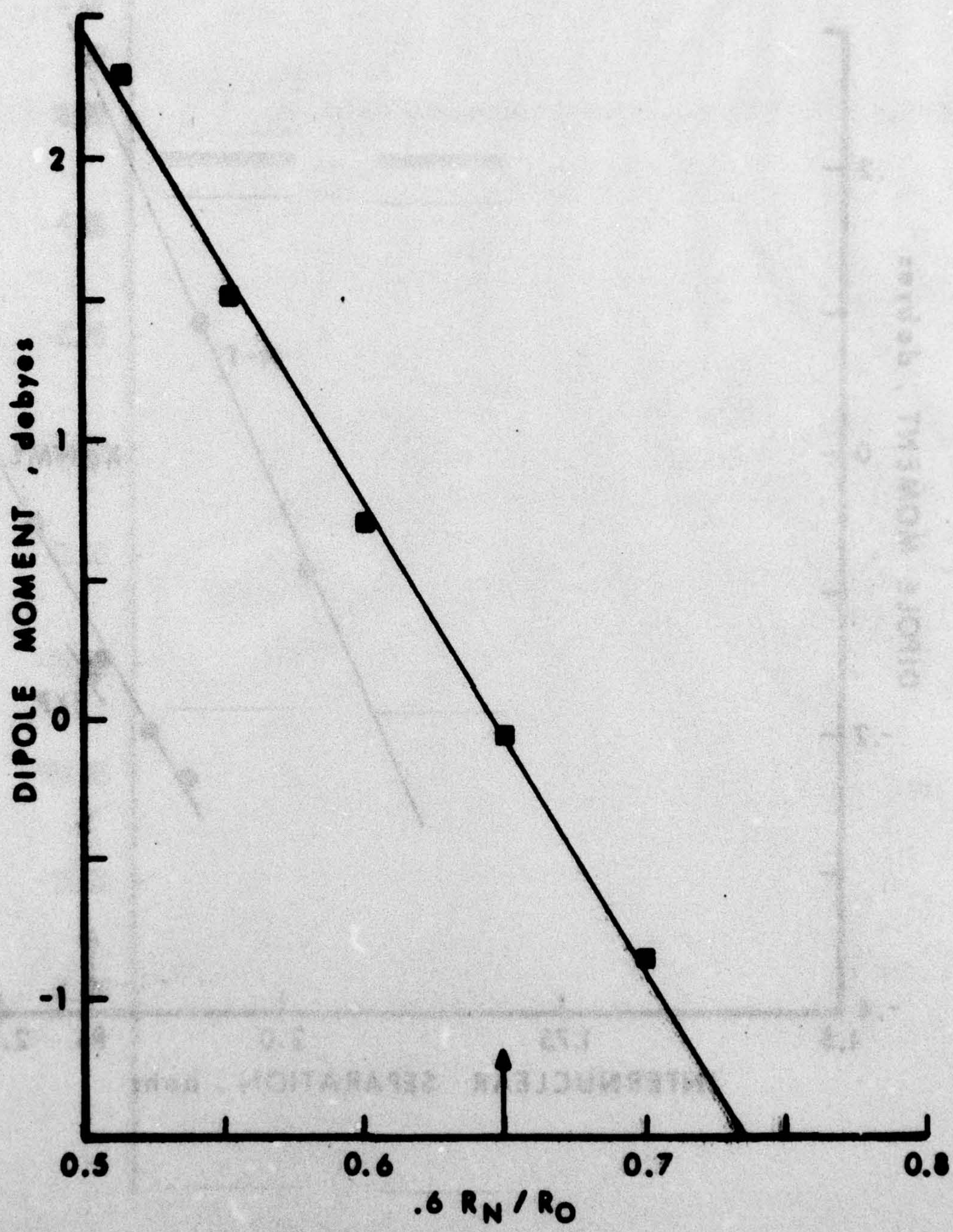

Figure 10. Dipole Moment as a Function of Ratio of Atomic Sphere Radii in NO.

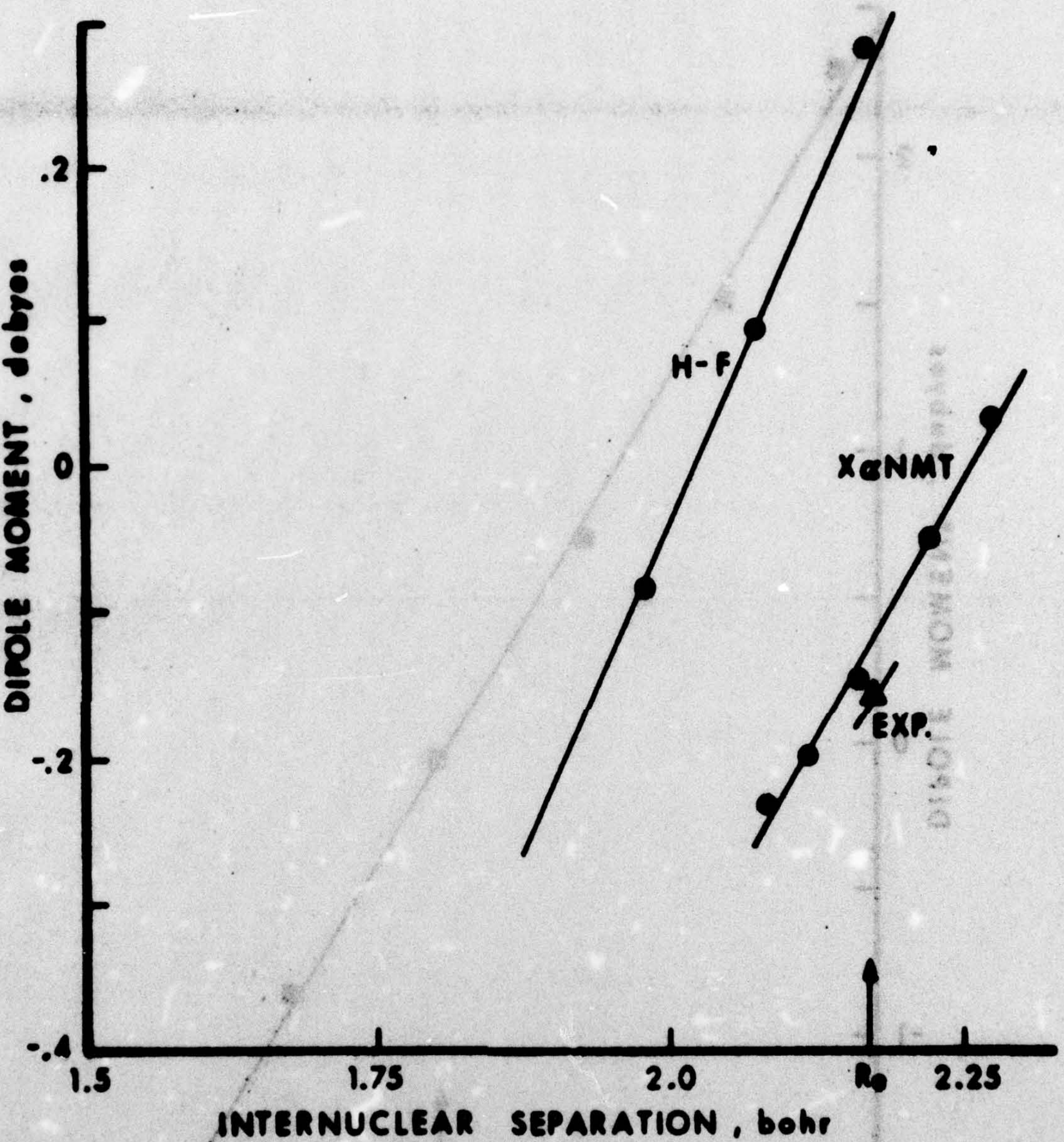

Figure 11. Dipole Moment as a Function of Internuclear Separation in NO.

C. Increasing the Accuracy of Total Energy Calculations.

The calculated excitations were in agreement with experiment. These excitations, however, are calculated as differences in total energy between a ground and an excited state. Although this energy difference may be sufficiently accurate, the actual energy of both states may be in error by a similar amount. For excitations, where there would be an error cancellation, this would be of little concern.

On the other hand, when calculating dissociation energies, one needs an accurate value of the energy of the ground state of the molecule. Now the energy difference is between the molecular ground state and the energy of the individual atoms when no longer found in a molecule, i.e., at infinite separation. Thus there is no longer the possibility of an error cancellation when comparing two molecular states both of which may be in error by a similar amount. The dissociation energy was disappointing even with the calculated energy-selected radii in which case it was 36% of the experimental value[33]. (Nevertheless, it was a definite improvement over the value of only 12% of experiment which was obtained with an outer-sphere radius corresponding to the equilibrium separation distance.) Increasing by one the number of partial waves used in the expansion resulted in a different, more negative total electronic energy. Varying the outer-sphere radius to determine if the minimum in energy still occurred at the same value of outer-sphere radius showed the total energy decreasing (Figure 12) until the minimum outer-sphere radius, just large enough to contain all atomic spheres, was used. The dissociation energy for NO was now 72% of experiment. Inclusion of one more term in the partial wave expansion improved this to 98% of the experimental value for NO.

The same procedure was used for CO with the results as shown in Table VIII.

Table VIII. Calculated Equilibrium Separations and Dissociation Energies for NO and CO.

Compound	Equilibrium Separation (bohr)		Dissociation Energy (eV)	
	Exp.	Calc.	Exp.	Calc.
NO	2.175	2.162	6.5	6.4
CO	2.132	2.142	11.1	11.3

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[33] G. Herzberg, op cit.

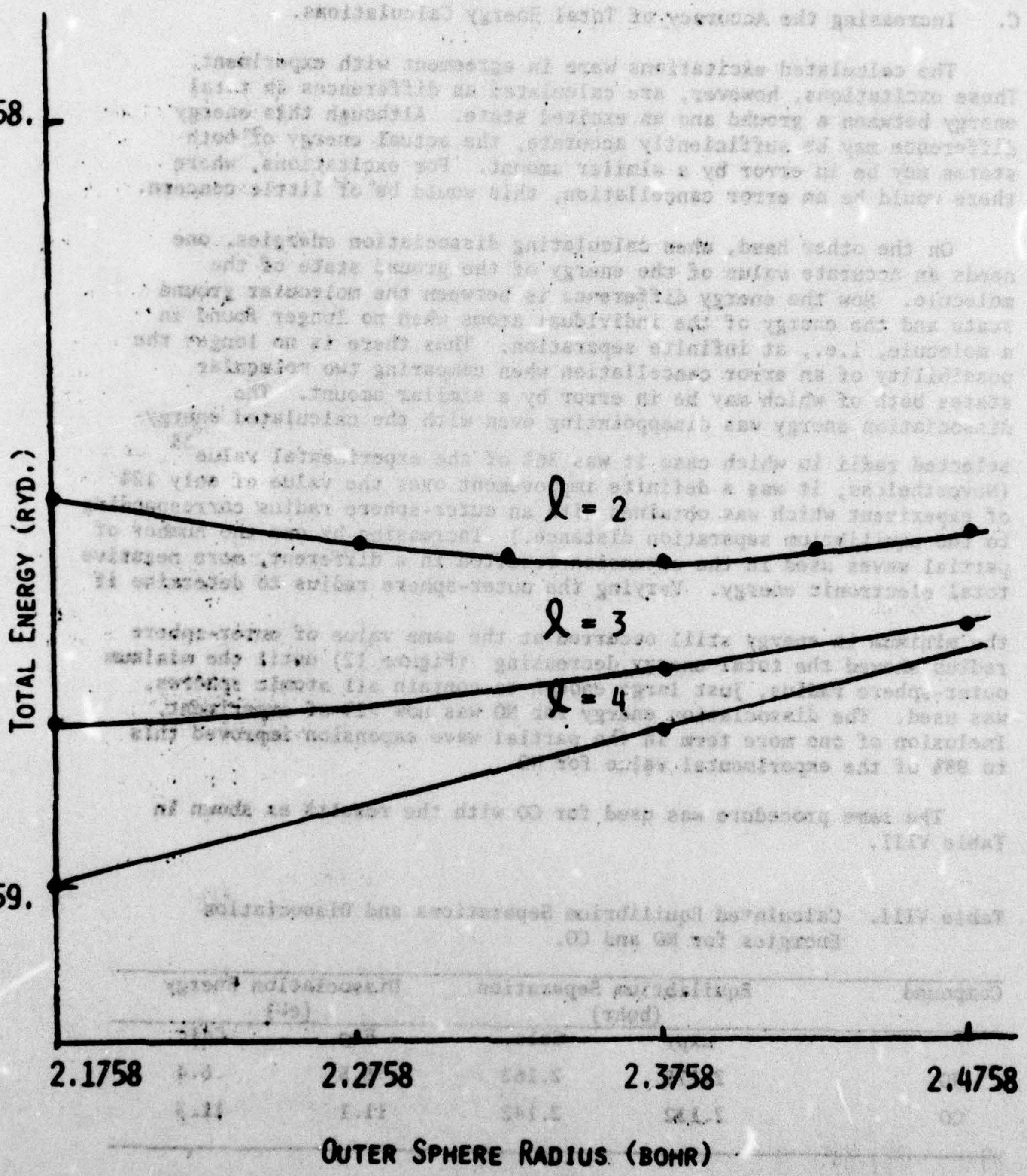

Figure 12. Total Energy as a Function of Outer Sphere Radius for $\ell=2,3,4$ in NO.

IV. CONCLUSIONS

Many calculated values of excitation energies and ionization potentials utilizing the multiple-scattering x-alpha method have been in good agreement with experiments. The inclusion of the NMT corrections which have the ability to account, to a certain extent, for non-muffin-tin portions of the potential has increased the usefulness of the method. The non-muffin-tin (NMT) corrections have predicted binding for molecules which were previously unbound in calculations using the muffin-tin potential.

The most important aspect of the present work is that a method was developed for performing accurate total energy calculations in the x-alpha method without the usual arbitrariness in selection of parameters. One needs simply to use relatively high ℓ-values (up to $\ell=4$ in NO, for example), choose the atomic spheres in the ratio of their Slater atomic radii, and use an outer sphere radius equal to the internuclear separation.

A systematic study of the dependence of the energy upon sphere radii and ℓ-values has yielded relationships for optimal choice of sphere radii should the use of large ℓ-values be undesirable. This study has also suggested a method for determining dipole moments of improved accuracy.

The practical application of all this is that the method now appears viable for the study of chemisorption processes so long as one includes NMT correction terms. A surface could be modeled as a cluster of metallic atoms, as schematically illustrated in Figure 13, while a gaseous species is allowed to approach. An accurate determination of the potential energy-curves for different chemisorption sites would yield the forces upon the gas. For different gaseous species, atoms and molecules, one could then determine relative metal-gas adsorption energies, preferred adsorption sites, and in the case of molecules, preferred orientation. An accurate calculation of dissociation energies is essential to the study of chemisorption and the chemical interactions of metal surfaces with gaseous species. The calculated values of dissociation energy for NO and CO provide an impetus for applying the method to metal-gas systems where the ability to obtain accurate values of these properties would be a significant step in the creation of a detailed microscopic theory of erosion.

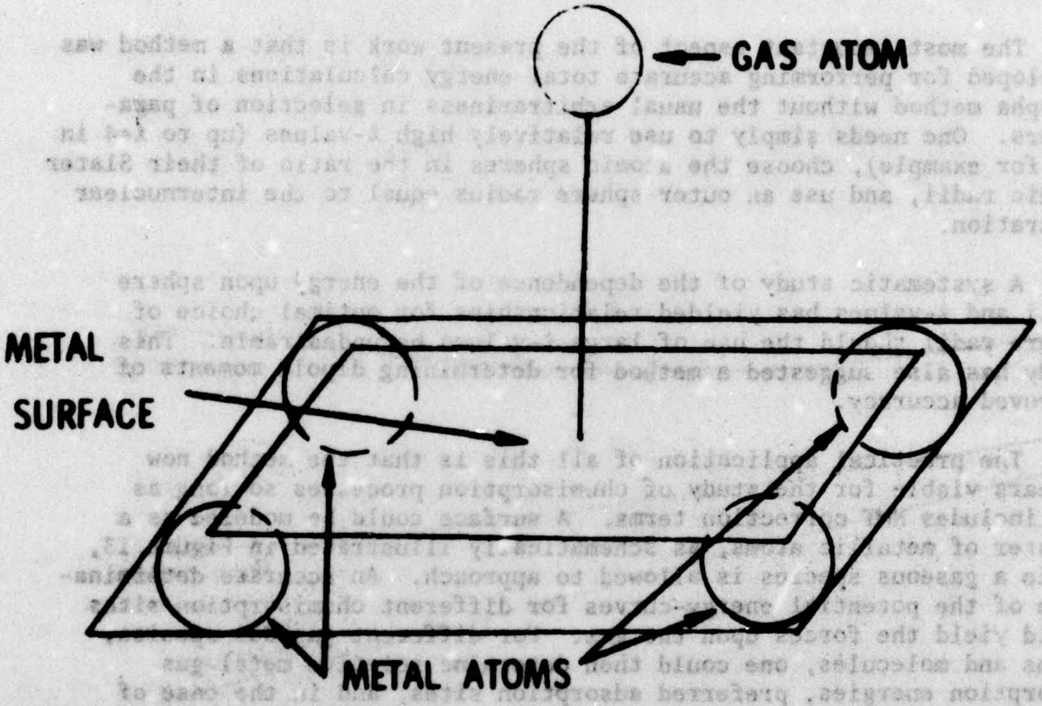

Figure 13. Gas Metal Surface Interaction (schematic).

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