NRL Report 6547

Anisotropy in Physical Adsorption on Graphite

July 31, 1967

NAVAL RESEARCH LABORATORY
Washington, D.C.

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ABSTRACT

Anisotropy of polarizability has been taken into account in calculating the relative strengths of adsorption of Ne, A, Kr, Xe, and CO_2 on several possible sites in the graphite lattice. A 6-12 potential, modified to include an angular dependence arising from anisotropy considerations, was summed over the lattice. As a direct result of the anisotropy, sites on the plane consisting of edges of basal planes exhibit a higher energy of adsorption at 0°K for all the gases considered. Calculations ignoring anisotropy have shown that the nature of the results depends markedly on this characteristic of graphite.

For the inert gases at -196°C, adsorption is still favored on the edge plane unless the adsorption is considered to be immobile. In contrast, for CO_2 at 0°C the entropy effect predominates and the basal plane offers the more favorable sites for adsorption. These calculations have ignored any unusual edge effects which may overwhelm the anisotropy effects; in the absence of such effects anisotropy is able to account for the existence of two types of sites on graphite, the relative stability of which depends on temperature.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problem C05-18
Project RR 001-01-43-4702

Manuscript submitted February 15, 1967.

ANISOTROPY IN PHYSICAL ADSORPTION ON GRAPHITE

INTRODUCTION

The polarizability of graphite is strongly anisotropic, having a value close to zero in a direction perpendicular to the basal planes, and a value of 3.42×10^{-24} cc/molecule along the C-C bond in the planes (1). Deitz has suggested that this anisotropy is responsible for two distinct arrays of sites for physical adsorption on graphite (2). The present work examines the theoretical basis for this suggestion, and extends the consideration of anisotropy to the adsorbate as well as the adsorbent.

Dispersion attraction depends on the polarizabilities of the interacting species. Because of graphite's anisotropy, we expect that an approaching adatom will be subjected to considerably different electronic environments depending on the direction of its approach to the crystal. If it approaches the basal plane, the resulting attraction is limited by the severely attenuated electronic oscillations perpendicular to the plane; if it approaches a crystal face composed of edges of basal planes (an edge plane*), the maximum polarizability is presented and the interaction may lead to a higher adsorption energy.

In comparing the energy of physical adsorption on the basal planes with that on the edge planes, four factors must be taken into account: (a) anisotropy of polarizability, (b) different distribution of carbon atoms, (c) different equilibrium distances of adatoms, and (d) unknown electronic states of carbon atoms in the edge plane. Computer programs have been set up to perform detailed summations over both aspects of a graphite crystal, taking anisotropy into account in obtaining the expression for dispersion interaction with an adatom. Using a modified 6-12 pairwise potential, repeated sums for incremental distances establish the equilibrium separation, and the first three of the above factors are considered. The possible unsaturation and/or unusual bonding of the edge atoms have been neglected.

Avgul and Kiselev (3) have mentioned the anisotropy of graphite in adsorption, but give no explanation of pertinent calculations. They state only a qualitative result, with which the present work does not agree.

Our consideration of anisotropy of polarizability follows that of de Boer and Heller (4) who have extended London's representation of interacting atoms as isotropic harmonic oscillators to the anisotropic case. If the component polarizabilities are $\alpha_1, \alpha_2, \alpha_3$, and the corresponding characteristic frequencies are ν_1, ν_2, ν_3, the expression for the dispersion interaction between anisotropic atoms is

$$E = -\frac{h}{4} \sum_{i=1}^{3} \sum_{k=1}^{3} C_{ik}^2 \frac{\nu_i \nu_k'}{\nu_i + \nu_k'} \alpha_i \alpha_k' \tag{1}$$

*There are at least two ways of cleaving the graphite crystal to produce an edge plane; we have chosen the one in which the cleavage is perpendicular to the basal planes and along a line which bisects opposite sides in a row of hexagons. The resulting "plane" is not strictly planar; a geometric plane on the crystal edge would have one half of the atoms in the plane, and one fourth displaced slightly to each side (see Fig. 2).

NOTE: This work carried out during tenure of NAS-NRC Postdoctoral Research Associateship

where the primes refer to a specified member of the interacting pair. The C_{ik} are the interaction energies of two unit dipoles with the directions of unit vectors **I** and **K**. If **R** is the vectorial distance between atoms,

$$C_{ik} = (1/R^3)[\mathbf{I} \cdot \mathbf{K} - (3/R^2)(\mathbf{I} \cdot \mathbf{R})(\mathbf{K} \cdot \mathbf{R})] \ . \tag{2}$$

Our analysis consists (a) of calculations of energies of adsorption at 0°K on both the basal plane and on the edge plane for an isotropic atom (the inert gases), and an anisotropic admolecule (CO_2), and (b) of an estimation of the relative stabilities of the two types of sites at temperatures above 0°K.

ISOTROPIC ADATOM

For the case of an inert gas atom adsorbed on the basal plane of graphite, we have the following relationships (primes refer to graphite): $\alpha_1' = 0$, $\alpha_2' = \alpha_3' = \alpha_{||}$, $\alpha_1 = \alpha_2 = \alpha_3 = \alpha$; and analogous relationships for the ν's. The subscript $||$ refers to the direction along the C-C bond in graphite. This allows us to write

$$A_{12} = A_{13} = A_{22} = A_{23} = A_{32} = A_{33} = A = \frac{h}{4} \frac{\nu\nu_{||}}{\nu + \nu_{||}} \alpha\alpha_{||} \ . \tag{3}$$

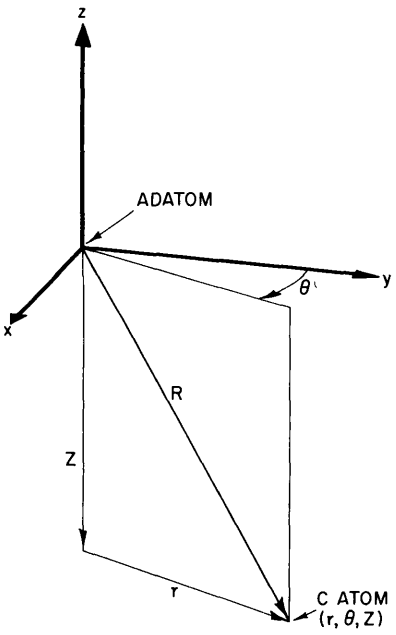

Fig. 1 - Coordinate system used to identify atoms of the graphite lattice

Since $\alpha_1' = 0$, $A_{11} = A_{21} = A_{31} = 0$, we need not concern ourselves with the corresponding C_{ik}.

To obtain a general expression for the dispersion interaction with any carbon atom of the lattice, we let the adatom be the center of a right cylindrical coordinate system, with its axis perpendicular to the graphite surface (see Fig. 1). Defining the z direction as positive toward the surface, we can write the following for the C_{ik} characteristic of the interaction of the adatom with the carbon atom with coordinates (r, θ, z):

$$C_{12} = (1/R^3)(-3rz \sin \theta/R^2)$$

$$C_{13} = (1/R^3)(-3rz \cos \theta/R^2)$$

$$C_{22} = (1/R^3)(1 - 3r^2 \sin^2\theta/R^2)$$

$$C_{23} = (1/R^3)(-3r^2 \sin \theta \cos \theta/R^2)$$

$$C_{32} = C_{23}$$

$$C_{33} = (1/R^3)(1 - 3r^2 \cos^2\theta/R^2)$$

where $R^2 = r^2 + z^2$.

Performing the indicated operations, we get

$$E = -A(2R^2 + 3r^2)/R^8 \tag{4}$$

for the interaction of an isotropic adatom on the basal plane with a carbon atom of the graphite lattice.

Construction of the coordinate system with the z axis perpendicular to the edge plane leads to the expression*

$$E = -A\,[2R^2 + 3(z^2 + r^2 \sin^2\theta)]/R^8 \,. \tag{5}$$

Combination of each of these with a repulsive term and summation over the lattice allows comparison of the strength of adsorption on the two planes. Similar sums, assuming the polarizability of the carbon atoms in graphite is isotropic, will isolate the role of anisotropy in the calculation.

Assuming an inverse-twelfth-power repulsion, we have for the total interaction of the adatom and a carbon atom located at (r, θ, z):

$$\Psi = -A\,(2R^2 + 3r^2)/R^8 + B/R^{12} \tag{6}$$

when adsorption is on the basal plane. Our evaluation of A and B makes use of Crowell's (5) method for obtaining an analytical expression for the interaction energy between an atom and a set of infinite basal planes from the pairwise potential between the solitary atom and individual atoms of the planes. It involves the assumption, which has been shown to be quite valid (5), that the basal plane may be treated as a homogeneous lamina exhibiting its characteristic density of carbon atoms. Thus, the pairwise potential may be integrated over the infinite plane. Crowell has further pointed out that the contribution of the planes other than the first may be taken into account with tabulated mathematical functions (whose derivatives are also tabulated), so that A and B may be evaluated in the usual way, given the equilibrium distance of the adatom and an experimental energy of adsorption.

The constant A is independent of anisotropy, and B is assumed so also. (This assumption is discussed later.) This allows insertion of the same A and B into the expression for the potential energy on the edge planes.

For the basal plane, the attractive term for the potential between a single atom and a single infinite plane is obtained by integrating the expression

$$A \int_{r=0}^{\infty} \int_{\theta=0}^{2\pi} (1/R^8)(2R^2 + 3r^2)\, r\sigma \; dr d\theta \tag{7}$$

where σ is the density of carbon atoms in the basal plane. Integration yields

$$(2\pi\sigma)(3A/4z^4) \,.$$

Integration of the inverse-twelfth-power repulsion over an infinite plane yields

$$(2\pi\sigma)(B/10z^{10})$$

where the z arises from the relation $R^2 = r^2 + z^2$.

Using Crowell's (6) notation, the expression for the total interaction of the adatom and semi-infinite set of basal planes is

*Changing the orientation of the coordinate system when considering adsorption on the edge plane is mathematically unnecessary, of course; it is possible to express all interaction energies in terms of one coordinate system. However, the necessary summations are far more readily accomplished by orienting the z axis perpendicular to the plane in question.

$$\phi = -2\pi\sigma \left[\frac{3A\,\Psi^{(3)}(x)}{24d^4} - \frac{B}{10z^{10}} \right] \tag{8}$$

where $x = z/d$ is the ratio of the distance of the adatom from the surface to the interplanar spacing in graphite, and $\Psi^{(n)}(x) = (d^{n+1}/dx^{n+1})\,\ell n\, x$. The latter functions have been tabulated by Davis (7) for $n = 1$ to 4. This expression and its derivative with respect to z allow evaluation of A and B from the equilibrium distance of the adatom and the experimental energy of adsorption. For the equilibrium distance we have used the sum of the radius of the adatom (8) and one-half the interplanar spacing in graphite; for the experimental energy at adsorption, we have used the experimental work of Sams, Constabaris, and Halsey (9), taking the energy of adsorption of argon on highly graphitized carbon (i.e., basal plane comprises the overwhelming majority of surface) at 0°K to be about 2100 cal/mole. This is the only experimental energy we have used; for neon, krypton, and xenon we have assumed that the attractive constant is proportional to the polarizability of the gas. Values of the attractive and repulsive constants are presented in Table 1.

Table 1
Attractive and Repulsive Constants for Ne, A, Kr, and Xe on Graphite

Gas	10^5 Å^6 cal/mole	10^9 Å^{12} cal/mole	Gas	10^5 Å^6 cal/mole	10^9 Å^{12} cal/mole
Ne	0.558	0.150	Kr	3.52	2.02
A	2.33	1.11	Xe	5.72	4.58

Computer programs* have been set up in FORTRAN to perform detailed sums for four cases of adsorption of an inert gas atom on graphite: (a) on the basal plane over the center of a hexagon, (b) on the basal plane directly over a carbon atom, (c) on the edge plane in the gap between layers, and, (d) on the edge plane directly over a carbon atom which juts out from the surface (see Fig. 2).

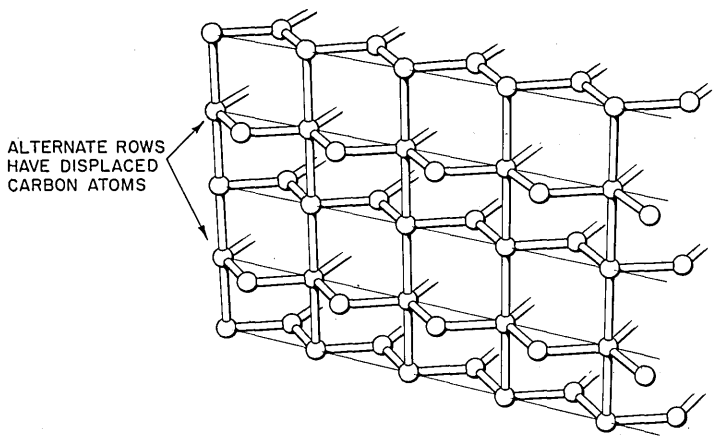

Fig. 2 - Schematic representation of an edge plane in the graphite lattice

*See Appendix A for explanations of all the programs used.

The calculated energies are presented in Table 2. The basal plane results are compared with the experimental values quoted by Crowell and Chang (10). In the light of present assumptions, inclusion of the zero point energy was not felt justified. Calculation of the zero point energy for argon gave between 65 and 70 cal/mole for all four positions; ignoring this will not affect our conclusions.

The results indicate that there is considerable energetic advantage to adsorption in the gap on the edge plane. That the advantage is the result of anisotropy is demonstrated in Table 3, where the same sums were performed for a lattice of isotropic carbon atoms.

Table 2
Results for Potential Summed as Indicated

Position	Ne		Ar		Kr		Xe	
	ϕ (cal/mole)	z_0 (Å)	ϕ (cal/mole)	z_0 (Å)	ϕ (cal/mole)	z_0 (Å)	ϕ (cal/Mole)	z_0 (Å)
Edge Plane								
C Atom	685	3.0*	2080	3.2*	2840	3.3*	3850	3.5*
Gap	980	2.2*	3050	2.3*	4110	2.4*	5450	2.6*
Basal Plane								
C Atom	700	3.1	2080	3.4	2800	3.5	3720	3.7
Hexagon	765	3.0	2160	3.4	2890	3.5	3790	3.7
Experiment†	729	3.1	2130	3.4	2790	3.5	3700	3.7

*Measured from the outermost set of C atoms.
†Taken from Ref. 11.

Table 3
Results for Argon Assuming the Polarizability of Graphite is Isotropic

Position	ϕ (cal/mole)	z_0 (Å)	Position	ϕ (cal/mole)	z_0 (Å)
Edge Plane			Basal Plane		
C Atom	1098	3.4	C Atom	2210	3.4
Gap	1815	2.5	Hexagon	2275	3.4

The basal plane results may be compared with those of Crowell and Young (11) for a detailed summation in the case of argon on graphite. They investigated the likelihood of a periodicity of energy on the basal plane by calulating an energy of adsorption for three different sites. Two of these are the same as ours: the center of a hexagon, and over a carbon atom, for which they calculated 1750 and 1710 cal/mole, respectively. Their values are lower than ours because of their assumption of a larger repulsive constant. They concluded that there is no reason to expect localized adsorption of argon on graphite.

Our results indicate that anisotropy contributes to the disparity between the two sites, but not sufficiently to alter the above conclusion for argon. Based on the hexagon values, our work gives 3.7% periodicity compared to Crowell and Young's 2.3%. In the case of neon, however, we calculate (neglecting quantum effects) a periodicity of 9.3%, which may be sufficient to cause observable localization.

The calculations of Avgul, et al. (12a, b) should be mentioned here, since they indicate a very high degree of periodicity in the basal plane for argon. However, this results from the assumption of an equilibrium distance over the hexagon which is considerably smaller than that over the other two positions considered. Neither the earlier work of Crowell and Young (11) nor the present work support this assumption.

It is of interest to compare the contribution of the first layer of atoms in the surface with the total interaction energy. The results for argon are presented in Table 4. The contribution of the first layer of edge atoms comprises a much smaller fraction of the total interaction than that of the first basal plane. In the case of adsorption over the gap in the edge plane, about half of the dispersion interaction arises from bulk atoms having no edge effects. This indicates that unusual bonding (i.e., a different value of the polarizability) in the edge atoms would have but a secondary effect on our results.

Table 4
Comparison of the Contribution of the First Layer of Atoms to the Total Energy

Position	Interaction Energy, ϕ (cal/mole)		Position	Interaction Energy, ϕ (cal/mole)	
	First Layer	Total		First Layer	Total
Edge Plane			Basal Plane		
C Atom	1410*	2080	C Atom	1980	2080
Gap	1680*	3050	Hexagon	1900	2160

*The first layer includes all boundary edge atoms even though they do not lie in a true plane.

The effect of possible unpaired electrons, or free radicals, on the edge atoms has not concerned us here. Although these might lead to a strong adsorption on the edges, we have shown that the existence of two types of sites on graphite does not require postulating this particularly high energy situation. In this regard it is worth mentioning recent work (13) which indicates that free radical centers in carbon have low chemical reactivity, probably a consequence of the pi character of the unpaired electrons, which would allow stabilization by resonance over neighboring carbon atoms. It is not likely, therefore, that unpaired electrons resulting from cleavage of a C-C bond are localized in the edge plane.

We feel the use of the same repulsive constant for the edge atoms and the basal plane atoms is reasonable. Repulsion arises from the Pauli exclusion principle; it depends not on the nature of the polarizability, but primarily on the size and shape of the electronic orbitals of the interacting species. In any case, we have carried out calculations assuming different values of the repulsive constant, and find that the energy varies by a factor of two when the constant is varied by a factor of three. This means that to overcome the effect of anisotropy, the repulsive constant for the edge would have to be more than twice that for the basal plane. Since it is more likely that repulsion is lower on the edge plane, where the adatom approaches from a direction of lower electron density, it is conservative to assume the repulsive constants equal.

ANISOTROPIC ADMOLECULE

The calculation of the adsorption energy for CO_2 on graphite is analogous to that for the inert gases, with the complication that the adsorbate is anisotropic as well as the adsorbent. More severe approximations must be made, but they are always internally consistent and should not affect the relative results for different orientations of the CO_2 and graphite.

In the development of the expressions for dispersion interaction we have assumed, for lack of a better approximation (14), that

$$\nu_{\perp} = \nu_{\parallel}$$

where the subscripts refer to perpendicular and parallel directions relative to the internuclear bonds in the admolecule.

Let us first consider the general case of a linear molecule adsorbed with an arbitrary orientation on the graphite surface. The values generally given for the components of the polarizability of a linear molecule are those based on a reference frame within the molecule, with the z axis coincident with the internuclear bonds, and the other two axes at right angles to it and to each other. In the present situation we must realize that the polarizability is a tensor, not a scalar, and treat it accordingly. That is, we must evaluate the polarizability tensor in the reference frame of the surface before we can take advantage of the equations developed by de Boer and Heller for the dispersion interaction between anisotropic oscillators.

In the reference frame of the admolecule, the polarizability tensor is

$$T = \begin{pmatrix} \alpha_{\perp} & 0 & 0 \\ 0 & \alpha_{\perp} & 0 \\ 0 & 0 & \alpha_{\parallel} \end{pmatrix} \tag{9}$$

If we construct a Cartesian coordinate system with the xy plane coincident with the surface, we can identify the orientation of the admolecule with the Eulerian angles ϕ, θ, and ψ. By matrix transformation we can express the polarizability tensor in terms of these angles relative to the reference frame of the surface as follows:

$$T_r = MTM'$$

where

$$M = \begin{pmatrix} \cos\psi\cos\phi - \sin\psi\cos\theta\sin\phi & \cos\psi\sin\phi + \sin\psi\cos\theta\cos\phi & \sin\psi\sin\theta \\ -\sin\psi\cos\phi - \cos\psi\cos\theta\sin\phi & -\sin\psi\sin\phi + \cos\psi\cos\theta\cos\phi & \cos\psi\sin\theta \\ \sin\theta\sin\phi & -\sin\theta\cos\phi & \cos\theta \end{pmatrix} \tag{10}$$

and M' is the transpose of M. Diagonalization of the resulting matrix gives the proper values of α to use in the dispersion equations.

Obtaining an expression for the general case does not seem justified at this time, so we have chosen five orientations which seem reasonable and yet allow simple use of the above procedure. Each orientation of the admolecule places it either perpendicular or parallel to the surface, resulting in values of 1 or 0 for the elements of M. The five

orientations and the resulting expressions for dispersion interaction are presented in Table 5. The symbol U represents the ratio of parallel to perpendicular polarizability components for the admolecule. Note that if U equals one, the equations reduce to those applicable to the inert gases.

Table 5
Five Orientations of Linear Admolecule and Associated Dispersion Interactions*

Case	Orientation	Expression for Dispersion Interaction
1	Parallel to the basal plane	$E = (A/R^6)[1 + U + 9z^2r^2/R^4 + (r^2/R^2)(9r^2/R^2 - 6)(\cos^2\theta + U \sin^2\theta)]$ (11)
2	Perpendicular to the basal plane	$E = (A/R^6)[2 - 6r^2/R^2 + (9r^2/R^4)(r^2 + Uz^2)]$ (12)
3	Parallel to the edge plane and perpendicular to the basal plane	$E = (A/R^6)[2 - 6(z^2 + r^2 \cos^2\theta)/R^2 + 9(z^2 + r^2 \cos^2\theta) \times (z^2 + r^2 \cos^2\theta + Ur^2 \sin^2\theta)/R^4]$ (13)
4	Parallel to the edge plane and parallel to the basal plane	$E = (A/R^6)\left\{1 + U + 3z^2/R^2 - 6Ur^2 \cos^2\theta/R^2 + 9r^2 \cos^2\theta[r^2 \sin^2\theta + U(z^2 + r^2 \cos^2\theta)]/R^4\right\}$ (14)
5	Perpendicular to the edge plane	$E = (A/R^6)[1 + U - 6(r^2 \cos^2\theta + Uz^2)/R^2 + 9(z^2 + r^2 \cos^2\theta)(r^2 + Uz^2)/R^4]$ (15)

*A is defined as before, using the perpendicular polarizability component of CO_2.

Combining each of these expressions with an inverse twelfth-power repulsion, it remains to evaluate the attractive and repulsive constants for the CO_2 molecule. The procedure is analogous to that for the inert gases; for the case of parallel adsorption on the basal plane, integration of the pairwise potential over an infinite plane, and inclusion of the rest of the lattice following Crowell (5,6) yields

$$(2\pi\sigma)\left(\frac{A\Psi^{(3)}(x)(3+U)}{32d^4} - \frac{B}{10z^{10}}\right)$$

for the potential between one CO_2 molecule and the graphite lattice.

Since there are no experimental data from which we can obtain the energy of adsorption of CO_2 on the basal plane at 0°K, we assume, as with the inert gases, that A is proportional to the polarizability of the adsorbate. Consistent with our definition of A and U for CO_2, we calculate the former from the value of A for one of the inert gases and the

perpendicular polarizability of CO_2. To evaluate B we must have a value for the equilibrium distance of approach to the surface for parallel adsorption on the basal plane. Because of the pi clouds in both CO_2 and graphite, we have assumed that to a first approximation the equilibrium distance is the same as the distance between planes in graphite, 3.35Å. This is reasonable, since the collision diameter of CO_2 is 4.4Å (8), and we expect the former dimension to be somewhat smaller than the latter. In carrying out the evaluation of A and B, we have further assumed that each atom in CO_2 may be treated independently; i.e., for dispersion purposes the atoms are indistinguishable, yet each maintains the anisotropic polarizability characteristic of the CO_2 molecule.

The resulting values of A and B are, respectively, 2.79×10^5 (cal/mole)Å^6, and 1.56×10^9 (cal/mole)Å^{12}.

Computer programs have been written in FORTRAN for the five cases in question (Table 5). In summing over the graphite lattice, the carbon-oxygen distance in CO_2 was taken to be 1.16 Å (15). As before, repeated sums were made for incremental distances, and the equilibrium distance for each case was taken as that corresponding to the energy minimum. The results are presented in Table 6. The absolute values of these figures should not be taken too seriously; their relationship to one another is what we want to examine.

Table 6
Energies of Adsorption of CO_2 on Planes of Graphite

Case	Orientation	ϕ (Kcal/mole)	z_0 (Å)
1	Parallel to basal plane	10.0	3.4
2	Perpendicular to basal plane	8.4	3.0*
3	Parallel to edge plane, perpendicular to basal plane	14.7	2.3
4	Parallel to edge plane, parallel to basal plane	14.8	2.3
5	Perpendicular to edge plane	10.8	2.0*

*The value of z_0 for the closest atom.

In both the parallel and perpendicular orientations, the edge atoms offer energetically more favorable adsorption sites than do the atoms in the basal plane. The advantage is about 5 kcal/mole for the parallel orientation and about 0.8 kcal/mole for the perpendicular orientation. Thus the conclusion for the inert gases, namely that the existence of two types of sites for physical adsorption may be accounted for by the anisotropy of graphite's polarizability, may be extended to the case of CO_2.

It is of interest to note the relative energies for adsorption parallel to the basal plane and perpendicular to the edge plane. The point has frequently been made (16) that when the two factors, anisotropy of polarizability and additivity of van der Waals' forces, oppose each other in the dispersion interaction between molecules, the latter predominates and leads to greater stability when the molecules are aligned side by side. If we were to consider a crystallite of graphite consisting of several layers of basal planes to be a huge "molecule," an exception to this general rule would occur. The alignment of maximum polarizability components (perpendicular adsorption on the edge plane) actually

produces more stability than alignment of the "molecular axes" (parallel adsorption on the basal plane).

Another point of interest is the comparison of adsorption energies calculated for CO_2 parallel to the basal plane by our detailed summation method and by Crowell's approximate method (5). We have used the same attractive and repulsive constants with both methods; the results are very close, as shown in Table 7, validating the use of Crowell's method of summing over the graphite lattice in this case. Crowell's method, however, can be used only for adsorption on the basal plane.

Table 7
Comparison of Crowell's Method to Exact Summation for Basal Plane

Case*	Adsorption Energy (Kcal/mole)		Case*	Adsorption Energy (Kcal/mole)	
	Crowell's Method	Exact Sum		Crowell's Method	Exact Sum
Both anisotropic	10.1	10.1	Case b	13.5	13.5
Case a	10.8	10.9	Case c	14.5	14.4

*The equilibrium distance from the surface was 3.4Å in every case.

We now examine the relative roles of the anisotropies of the adsorbate and the adsorbent in this system. ("Anisotropy" in this discussion implies "anisotropy of polarizability".) We have repeated the analysis for three hypothetical cases: (a) graphite anisotropic with CO_2 isotropic, (b) graphite isotropic with CO_2 anisotropic, and (c) graphite isotropic with CO_2 isotropic. The expression for attraction is different in each case, as are the attractive and repulsive constants. (See Appendix B for constants used.) The results are shown in Table 8. The anisotropy of graphite is clearly dominant in establishing the character of the results. In fact, it reverses the qualitative results for the edge plane and the basal plane: When graphite is considered anisotropic, the edge plane is energetically more favorable; when it is assumed isotropic, the reverse is true. The most likely reason for this reversal is the opposing effects of anisotropy and of the distribution of carbon atoms. The anisotropy favors the edge plane; the distribution, the basal plane. If anisotropy is ignored, the higher density of carbon atoms in the basal plane predominates; however, the effect of anisotropy is such that it overcomes this and leads to an even greater adsorption energy for the edge plane.

The effect of the anisotropy of CO_2 is relatively unimportant. Comparing the results of case (a) with the original results, we see (Table 8) that for the parallel orientations higher energies are obtained for the isotropic case, while for the perpendicular orientations higher energies are obtained for the anisotropic case. This is expected, since the polarizability of CO_2 is greater along the internuclear axis than perpendicular to it. The difference is greatest for the orientation perpendicular to the basal plane and smallest for the orientation parallel to the edge plane.

According to the present model, rotation of the CO_2 molecule in a plane parallel to the basal plane would encounter relatively little resistance. However, there is a barrier to rotation in a plane perpendicular to the basal plane, since the CO_2 molecule in the parallel orientation must acquire energy to assume the perpendicular orientation. If we let the molecule spin freely at a fixed distance from the surface, we can estimate its energy of adsorption and its equilibrium distance by taking the average of the parallel and

Table 8
Effect of Ignoring Anisotropy for CO on Graphite

Case	Orientation	ϕ (Kcal/mole)				z_0 (Å)			
		Case (a)	Case (b)	Case (c)	Original Results*	Case (a)	Case (b)	Case (c)	Original Results*
1	Parallel to basal plane	10.9	13.5	14.4	10.0	3.4	3.4	3.4	3.4
2	Perpendicular to basal plane†	6.5	10.9	8.6	8.4	3.1	3.0	3.1	3.0
3	Parallel to edge plane, perpendicular to basal plane	15.0	10.5	11.2	14.7	2.3	2.5	2.5	2.3
4	Parallel to edge plane, parallel to basal plane	15.1	10.7	11.5	14.8	2.3	2.5	2.5	2.3
5	Perpendicular to edge plane†	9.3	8.6	7.1	10.8	2.1	2.2	2.3	2.0

*Values taken from Table 6.
†The value of z_0 for closest atom.

perpendicular energies as a function of distance. This results in an energy of 7.5 kcal/mole at a distance of 4.1Å for a freely rotating molecule.

EXTENSION OF RESULTS TO TEMPERATURES ABOVE 0°K

Comparison of the relative stabilities of molecules adsorbed on these two faces of graphite based on this type of calculation is valid only at absolute zero, when entropy considerations do not enter the picture. However, estimates of the relative attraction of the basal plane and edge plane for an admolecule at finite temperatures are readily made after reasonable assumptions regarding the nature of the adsorbed layer in each case.

Inert Gases

We assume that there is complete freedom of translation on the basal plane and consider two cases on the edge plane: complete immobility, and freedom of translation in one dimension. The latter would result from an adatom's ability to slide along in the gap between basal planes. A third possibility is complete freedom of translation on the edge plane, in which case there would be no entropy difference for equal areas of basal and edge planes, and the only consideration beyond the absolute zero case would be the effect of temperature on our calculated energies. Since we assume that this effect may be ignored to a first approximation, we ignore this third possibility.

We must choose a standard state in order to compare the adsorbed layers on the two planes. Following de Boer (17), we pick a state in which the distance between adsorbed atoms at 0°C is the same as in the three-dimensional gas at one atmosphere and the same temperature. This results in a standard area of $4.08T \times 10^{-16}$ cm^2/atom. Analogous reasoning for the case of one-dimensional freedom yields a standard length of $1.22T \times 10^{-9}$ cm/atom. These values allow calculation of two- and one-dimensional translational entropies from the respective partition functions for the inert gases. The contribution of a vibration perpendicular to the surface is small enough to neglect for

our purposes. The only other entropy consideration is a configurational entropy for the case of immobile adsorption. This is readily calculated from the standard coverage and the expression

$$S^0_{config} = -R \ln \frac{\theta}{1-\theta}$$

where θ is the fractional surface coverage.

In the case of complete immobility on the edge plane, the entropy change for the process

adatom on basal plane (1 mole, 77°K, standard state)

adatom on edge plane (1 mole, 77°K, standard state)

consists of the loss of entropy corresponding to two degrees of translational freedom and the gain of the configurational entropy associated with immobile adsorption. Values are presented for the inert gases in Table 9.

Table 9
Entropy Changes for the Inert Gases Assuming Immobile Adsorption on Edge

Gas	ΔS^0_{tr} (eu)	ΔS^0_{config} (eu)	ΔS^0_{total} (eu)
Ne	-18.6	6.4	-12.2
A	-20.0	5.7	-14.3
Kr	-21.5	5.4	-16.1
Xe	-22.3	5.0	-17.3

If we now consider the case of one-dimensional freedom of translation on the edge, the entropy change for the above process consists of the loss of one degree of translational freedom without the gain of configurational entropy. Values for this case are presented in Table 10.

Table 10
Entropy Changes for the Inert Gases Assuming One Translational Degree of Freedom on Edge

Gas	ΔS^0 (eu)	Gas	ΔS^0 (eu)
Ne	-9.6	Kr	-11.0
A	-10.3	Xe	-11.5

We can now estimate the standard free energy change for the transfer of 1 mole of inert gas from the basal plane to the edge plane in the two cases, and get an idea of the relative stability of the adatom on the basal plane and the edge plane at liquid nitrogen temperatures. These results are presented in Table 11. We cannot conclude that either plane is heavily favored in any situation. All the values are less than 1 kcal/mole. If adsorption on the edge plane is immobile, then adsorption is favored on the basal plane except in the case of xenon. For the other inert gases, raising the temperature to 77°K causes an entropy gain on the basal plane which is sufficient to overcome the energy advantage in adsorption on the edge plane. If the adatom enjoys a degree of translational

freedom on the edge plane, the latter is favored except in the case of neon. For the other gases the increase in entropy on the edge plane is enough to maintain its advantage as the temperature is raised. The significance of these free energy differences is more readily apparent if they are converted to equilibrium constants. For example, the ratio of concentrations of xenon on the edge and basal planes in the second case is about 150 to 1. For argon, the same ratio is 2 to 1.

Table 11
Standard Free Energy Changes for Basal Plane to Edge Plane for Inert Gases

Gas	ΔF^0 (cal/mole)		Gas	ΔF^0 (cal/mole)	
	Immobile	One-Dimensional Translation		Immobile	One-Dimensional Translation
Ne	720	520	Kr	10	-370
A	210	-100	Xe	-330	-780

Carbon Dioxide

The calculation of entropy changes for CO_2 is analogous to that for the inert gases, with the inclusion of rotation considerations. In addition to the previous assumptions, we let the CO_2 molecule rotate in one dimension on the basal plane and restrain it from rotating on the edge plane. The latter assumption results from the existence of a physical well, in addition to a potential well for adsorption of CO_2 on the edge plane (see Fig. 2). The contribution of the degree of rotational freedom to the entropy on the basal plane is readily calculated from the one-dimensional rotational partition function for CO_2.

Since Deitz (2) has observed the presence of a small fraction of high energy sites for the adsorption of CO_2 on graphite at 0°C, we have chosen this temperature for the estimation of a standard free energy difference between the two types of sites under consideration here. The results are presented in Table 12.

Table 12
Standard Entropy and Free Energy Changes for Basal Plane to Edge Plane for CO_2

Character of Adsorption on the Edge Plane	ΔS^0 (eu)	ΔF^0 (cal/mole)
Immobile	-22.0	1220
One degree of translation	-20.9	900

In both cases considered, the basal plane is favored. In other words, the entropy effect upon raising the temperature to 0°C has overcome the energy advantage to adsorption on the edge plane. The assumption that the energy difference between the two types of sites is the same at 0°C as that calculated for 0°K is an oversimplification, but the qualitative conclusion is not affected. The energy difference would be smaller at 0°C, resulting in a higher positive standard free energy change.

Only if the CO_2 molecule is allowed to move as freely on the edge plane as it does on the basal plane will the advantage of adsorption on the edge plane be maintained as the

temperature is raised. However, it is only in the gaps of the edge plane that the admolecule finds a more stable site; this means that in order to gain entropy on the edge plane, some of the energy advantage must be sacrificed.

The stability of the edge plane relative to the basal plane at absolute zero is, on the basis of the models described, lost as the temperature is raised to 0°C. Thus the consideration of anisotropy of polarizability is not enough to account for the existence of two types of sites with greatly different stabilities for CO_2 adsorption at this temperature. The high energy sites observed for this system (2) are possibly due to unsaturated bonds or other edge effects at the boundaries of the basal planes of graphite.

CONCLUSIONS

Quantitative calculations of the effect of the anisotropy of polarizability in physical adsorption on graphite have been made for the first time. The anisotropy results in quite different energies of adsorption for the basal planes and the edge planes, the latter being favored in all cases at 0°K. It also contributes to the periodicity of energy on the basal plane; i.e., the calculated difference in energy between adsorption above the hexagon and that above a carbon atom is greater when the anisotropy of polarizability is taken into account than when it is ignored.

In the case of adsorption of an anisotropic molecule on graphite, the anisotropy of the molecule is relatively unimportant. However, if the anisotropy of the graphite is ignored, the calculated relative stability of adsorption on the basal and edge planes is reversed, and the basal plane seems to exhibit a higher adsorption energy than the edge plane.

Consideration of the effect of entropy on the relative stability of the two types of sites at liquid nitrogen temperature does not change the character of the results for the inert gases, unless adsorption on the edge plane is considered immobile. In the case of CO_2 at 0°C, however, the entropy effect dominates and the basal plane offers the more favorable sites.

It should be emphasized that the present calculations have ignored unusual edge effects which may in fact overwhelm the anisotropy effect. We have shown that, in the absence of edge effects, anisotropy is able to account for the existence of two types of sites on graphite, the relative stability of which depends on temperature.

ACKNOWLEDGMENTS

Thanks are due to Dr. Victor R. Deitz for suggesting this problem, and for many helpful discussions during the course of the calculations. We are also indebted to Messrs. Robert M. Mason and Arthur J. Ziffer of the Research Computation Center and Burton N. Navid of the Mathematical Physics Branch who gave freely of their time whenever they were called upon for assistance.

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Appendix A

EXPLANATION OF COMPUTER PROGRAMS

The computer programs used are set forth herein, along with the logic used in developing them and explanations of the symbols used in each.

In each case, calculations are repeated for chosen increments of distance from the surface between chosen limits. Printout includes attractive, repulsive, and net interaction energies and the distance of the adatom from the surface.

1. INERT GAS ADSORBED ABOVE THE CENTER OF A HEXAGON IN THE BASAL PLANE*

The expression to be summed is

$$\frac{-A\,(2R^2 + 3r^2)}{R^8} + \frac{B}{R^{12}}$$

where R is the distance between the adatom and the carbon atom in question, and r is the projection of R in the basal plane of this carbon atom.

Advantage is taken of the sixfold symmetry of the basal plane in this situation. The contributions of the first ten successive concentric "rings" are summed for each of the first ten basal planes. (The first "ring" is the hexagon in question, the second consists of the "outer" carbon atoms of the six hexagons enclosing the first, and so on.) Calculations need be made for but one-sixth of the plane, then multiplied by six. Three straight lines are drawn on the hexagonal lattice, intersecting at the center of the hexagon in question, and bisecting opposite sides of it. In addition to these lines, another is drawn which bisects the segment of the plane on which we shall focus our attention for the purposes of this summation. This line is called the "base line."

Three subscripts are used to locate a carbon atom: N is the number of the "ring" to which it belongs, I labels its position relative to the base line, and J denotes the basal plane in which it resides. Thus, quantities referring to the (N, I, J) th carbon atom are written $G(N, I, J)$.

Definitions of Symbols in the Program

ALPHA	Attractive Constant
B	Repulsive Constant
Q(N,I)	Number of equivalent carbon atoms (N, I)
Z(J)	Perpendicular distance from the adatom to the Jth plane

*The logic upon which this summation procedure is based is due to Mr. Robert M. Mason of the Research Computation Center.

S(N,I)	The value of r for the carbon atom on the base line in the Nth "ring"
RR(N,I)	The square of the distance, r, to the (N,I)th carbon atom
R(N,I)	r for the (N,I)th carbon atom
Y(N,I,J)	R for the (N,I,J)th carbon atom
E(N,I,J)	Attractive energy for the (N,I,J)th carbon atom
RE(N,I,J)	Repulsive energy for the (N,I,J)th carbon atom
EP(N,1)	Attractive energy up to the Nth "ring" for the first basal plane
REP(N,1)	Repulsive energy up to the Nth "ring" for the first basal plane
EP2(J)	Attractive energy up to the Jth plane
REP2(J)	Repulsive energy up to the Jth plane
ETOT	Total attractive energy
RETOT	Total repulsive energy
EFIN	Total interaction energy

2. INERT GAS ADSORBED ABOVE A CARBON ATOM IN THE BASAL PLANE

The expression to be summed is the same as in Program 1. In this situation, use of a threefold symmetry is made. Given the hexagonal lattice of the basal plane, concentric equilateral triangles are drawn about the carbon atom directly below the adatom, such that every atom of the lattice is included in a side or vertex of a triangle. Two sets result, labeled P and Q, each at a constant interval. The atoms belonging to each of these sets are further subdivided into those located at vertices and those on sides of triangles. The contributions of the members of these four sets of carbon atoms to the total interaction energy are readily expressed in terms of N, I, and J. These subscripts have functions analogous to Program 1: N refers to a particular triangle, I to the location of a carbon atom along the side of a triangle, and J to the basal plane in question.

Definitions of Symbols in the Program

ALPHA	Attractive Constant
B	Repulsive Constant
Z(J)	Perpendicular distance from the adatom to the Jth plane
DPO(N) DQO(N)	Distance from a point below the adatom to the vertex of the Nth triangle of set P or Q
SP(N) SQ(N)	Number of carbon atoms per side of the Nth triangle of set P or Q
YPO(N,J) YQO(N,J)	Distance from the adatom to the (N,J)th carbon atom in set P or Q (these are vertex atoms)
EPO(N,J) EQO(N,J)	Attractive energy corresponding to the above atom
REPO(N,J) REQO(N,J)	Repulsive energy corresponding to the above atom
P(N,I) Q(N,I)	Square of the distance from a point below the adatom to the Ith atom of triangle N in set P or Q

DP(N, I) DQ(N, I)	Distance from a point below the adatom to the Ith atom of triangle N in set P or Q (these are side atoms)
YP(N, I, J) YQ(N, I, J)	Distance from the adatom to the (N, I, J)th atom of set P or Q
EP(N, I, J) EQ(N, I, J)	Attractive energy corresponding to the above atom
REP(N, I, J) REQ(N, I, J)	Repulsive energy corresponding to the above atom
EPT(N, J) EQT(N, J)	Contribution to the total attraction of all side atoms of set P or Q up to the Nth triangle of the Jth plane
REPT(N, J) REQT(N, J)	Contribution to the total repulsion of all side atoms of set P or Q up to the Nth triangle of the Jth plane
ETOTP(N, J) ETOTQ(N, J)	Contribution to the total attraction of the side atoms and vertex atoms of set P or Q up to the Nth triangle of the Jth plane
RETOTP(N, J) RETOTQ(N, J)	Contribution to the total repulsion of the side atoms and vertex atoms of set P or Q up to the Nth triangle of the Jth plane
EEE(J)	Attractive energy of the carbon atom directly beneath the adatom
RRR(J)	Repulsive energy of the carbon atom directly beneath the adatom
ETOTJ(J)	Total attractive energy of the Jth plane excluding the carbon atom beneath the adatom
RETOTJ(J)	Total repulsive energy of the Jth plane excluding the carbon atom beneath the adatom
ETOT	Total attractive energy
RETOT	Total repulsive energy
EFIN	Total interaction energy

3. INERT GAS ADSORBED ABOVE A CARBON ATOM ON THE EDGE PLANE, AND ABOVE THE GAP ON THE EDGE PLANE*

The expression to be summed is

$$\frac{-A[2R^2 + 3(z^2 + r^2 \sin^2\theta)]}{R^8} + \frac{B}{R^{12}}$$

where the symbols are defined in Fig. 1 of the text. It was found more convenient to use rectangular coordinates in the summation, so the substitutions $b = r \sin\theta$ and $a = r \cos\theta$ were made.

Two locations were included in one program in this case because of the similarity of the manipulations required. However, in this explanation each case is considered separately.

First, let us take the adatom adsorbed directly over the carbon atom that juts out from the edge plane (see Fig. 2). The graphite lattice may be considered as a set of six types of planes of atoms, the planes taken perpendicular to the basal plane and parallel to the face shown in Fig. 2. That is, the 1st, 7th, 13th, etc.; the 2nd, 8th, 14th, etc.; the

*Translation of the logic of this summation into FORTRAN is due to Mr. Robert M. Mason of the Research Computation Center.

3rd, 9th, 15th, etc.; etc., are identical. Let N identify the plane of interest. The procedure is to locate each atom in the Nth plane for the six different types of planes.

If B is the distance across a hexagon (i.e., between atoms 1 and 3 of the ring), and A is the interplanar spacing, we can define units of distance in the a and b directions which are convenient for the summation in terms of N, A or B, and a subscript variable. For example, the distance in the b direction to the Ith atom may be written

$$B(N, I) = (I - 1)B, \quad I = 1, 2, 3, \ldots, \quad \text{for } N = 1, 3, 5, \ldots$$

$$B(N, I) = B/2 + (I - 1)B, \quad I = 1, 2, 3, \ldots, \quad \text{for } N = 2, 4, 6, \ldots .$$

Similarly, the distance in the a direction to the Jth atom may be written

$$A(N, J) = 2(J - 1)A, \quad J = 1, 2, 3, \ldots, \quad \text{for } N = 1, 4, 7, 10, \ldots$$

$$A(N, J) = (J - 1)A, \quad J = 1, 2, 3, \ldots, \quad \text{for } N = 2, 5, 8, 11, \ldots$$

$$A(N, J) = (2J - 1)A, \quad J = 1, 2, 3, \ldots, \quad \text{for } N = 3, 6, 9, 12, \ldots .$$

Symmetry is taken advantage of whenever possible; its degree differs for different locations in each plane. It is thus defined as a function of all three subscript variables; Q(N, I, J) gives the number of equivalent atoms with the same values of N, I, and J. For example,

When $N = 1, 5, 7, 11, 13, \ldots,$

$$Q(N, 0, 0) = 1$$

$$Q(N, 0, J) = 2, \quad \text{if } J \neq 0$$

$$Q(N, I, 0) = 2, \quad \text{if } J \neq 0$$

$$Q(N, I, J) = 4, \quad \text{if } J \neq 0 \text{ and } I \neq 0.$$

Analogous expressions are needed for three other sets of planes; these are in the program.

Definitions of Symbols in Program for Adsorption Over a Carbon Atom

ALPHA	Attractive Constant
BB	Repulsive Constant
A	Unit of distance in the a direction
B	Unit of distance in the b direction
C	B/2
D	Distance between successive edge planes
K	Upper limit to J
NN	Upper limit to N
M	Upper limit to I
Z	Distance to the first plane
LB(N, I)	Distance in the b direction to the (N, I) th location
LA(N, J)	Distance in the a direction to the (N, J) th location

Q(N, I, J)	Number of equivalent atoms with subscripts N, I, and J
F(N)	Square of the distance from the adatom to the Nth plane
LR(N, I)	Projection of R on the ab plane
R(N, I, J)	Distance from the adatom to the (N, I, J)th atom
ET(N, I, J)	Attractive energy of the (N, I, J)th atom(s)
RET(N, I, J)	Repulsive energy of the (N, I, J)th atom(s)
E(N)	Attractive energy of the Nth plane
RE(N)	Repulsive energy of the Nth plane
ED(N)	Net interaction energy of the Nth plane
ETOT	Total attractive energy
RETOT	Total repulsive energy
EFIN	Total interaction energy

Now, let us consider the case wherein the adatom is located above the gap between basal planes. The displacement from one of the basal plane edges is fixed arbitrarily at 2.47Å, so that the adatom is approximately equidistant from its three nearest carbon neighbors. The logic involved is analogous to that used above; however, the displacement from the basal plane by an arbitrary distance destroys the symmetry in one direction. To account for this, the sum is split into two parts: the contributions of those atoms "north" of the adatom, and of those "south" along a direction perpendicular to the basal planes.

Since there is no displacement in the b direction, the symmetry in that direction is retained.

Definitions of Symbols in Program for Adsorption Over the Gap

The symbols are for the most part the same as above; the distinction being a P appended to each symbol. New symbols are:

LEP (N, J)	Distance in the a direction to the (N, J)th location, the a direction having opposite sense from that in the definition of LAP(N, J)

Those terms which have a 2 appended to the symbol refer to that half of the graphite lattice for which LEP(N,J) replaces LAP(N,J).

To examine the effect of the anisotropy of graphite on the results of the inert gas summations, the energy expressions are replaced by simple 6-12 expressions with appropriate values of the attractive and repulsive constants.

4. CO_2 ON ANISOTROPIC GRAPHITE, ADSORBED PARALLEL TO THE BASAL PLANE WITH THE CARBON ATOM ABOVE THE CENTER AND THE OXYGEN ATOMS DIRECTED TOWARD THE SIDES OF A HEXAGON

The expression to be summed is

$$-(T/R^6)[(1+U+9z^2r^2/R^4) + (r^2/R^2)(9r^2/R^2-6)(\cos^2\theta + U\sin^2\theta)] + F/R^{12}$$

where T and F are the attractive and repulsive constants, and the other variables are defined in Fig. 1 of the text. For computational purposes, the substitutions $a = r \sin\theta$ and $b = r \cos\theta$ are made.

In this case, the basal plane is split into quadrants by an a axis, which passes through the center of a hexagon and opposite carbon atoms, and a b axis, which intersects the a axis at right angles at the center of a hexagon. The summation for the carbon atom of CO_2 may be worked out for one quadrant and multiplied by four; added to this must be the contributions of the graphite atoms located on the a axis. The summations for the oxygen atoms are done for one-half the plane and doubled; to this must also be added the contributions of the graphite atoms on the a axis.

The basal plane may be considered to be made up of four sets of rows of carbon atoms, a row of each set being a multiple of a fixed distance from the b axis. If the sets are labeled G, P, R, and B, and convenient unit distances are chosen as before, expressions for the distance from the point (X,Y) to the (I,J) th atom of each set are readily written down. For example,

$$[G(I,J)]^2 = [B/2 - X + (I-1)B]^2 + [C - Y + (J-1)A]^2$$

$$[P(I,J)]^2 = [B - X + (I-1)B]^2 + [2C - Y + (J-1)A]^2$$

etc. Combination of these distances with the distance from the adatom to the plane in question enables the evaluation of R for substitution into the proper energy expression.

Definitions of Symbols in the Program

T	Attractive Constant
F	Repulsive Constant
XC YC	Displacement of the carbon atom of CO_2 from the center of the hexagon in the b or a direction
XE YE	Displacement of one oxygen atom of CO_2 from the center of the hexagon in the b or a direction
XEP	Displacement of the other oxygen atom of CO_2 from the center of the hexagon in the b direction
Z	Distance of the adatom from the basal plane
D	Interplanar spacing in graphite
A	Distance between successive rows in the G, P, R, or Bth set of carbon atoms
B	Distance between the 1st and 3rd carbon atoms of a hexagon
NN	Upper limit to N
K	Upper limit to J
M	Upper limit to I
Q	Upper limit of the range of distances from the surface for which calculations are desired
U	Ratio of the parallel to perpendicular components of polarizability for CO_2
C	Distance between the b axis and the first row of carbon atoms

The following notation is used in the program: the final C indicates the carbon atom of the CO_2 molecule; the final E indicates the oxygen atom of the CO_2 molecule; the final

EP or E2P is used when the oxygen atoms of the CO_2 molecule are not equivalent with respect to the lattice; the letters G, P, R, and B refer to the corresponding sets of carbon atoms in the lattice. Only the symbols referring to cases C and G will be explicitly defined below.

LBG2C(I)	Distance squared along the b axis to the Ith location of set G from the carbon atom of CO_2
LAG2C(J)	Distance squared along the a axis to the Jth location of set G from the carbon atom of CO_2
LAVPC2(J)	Distance squared along the a axis to the Jth location of set P on the a axis from the carbon atom of CO_2. (Only carbon atoms of sets P and R find themselves on the a axis.)
LBVE2	Distance squared along the b axis to any carbon atom located on the a axis from either oxygen atom of CO_2
F2(N)	Distance squared from the molecule to the Nth basal plane
RGC2(N, I, J)	Distance squared from the carbon atom of CO_2 to the (N,I,J)th location of set G
REIC(N,I,J)	Repulsive energy of the (N,I,J)th carbon atoms interacting with the carbon atom of CO_2
EGC(N,I,J)	Attractive energy of the (N,I,J)th carbon atom of set G interacting with the carbon atom of CO_2
RVPC2(N,J)	Distance squared from the carbon atom of CO_2 to the (N,J)th carbon atom of set P on the a axis
EVPC(N,J)	Attractive energy of the (N,J)th carbon atom of set P on the a axis interacting with the carbon atom of CO_2
REIVC(N,J)	Repulsive energy of the (N,J)th carbon atoms on the a axis interacting with the carbon atom of CO_2
EC(N)	Attractive energy of all carbon atoms in the Nth plane not on the a axis with the carbon atom of CO_2
REC(N)	Repulsive energy of all carbon atoms in the Nth plane not on the a axis with the carbon atom of CO_2
EVC(N)	Attractive energy of all carbon atoms in the Nth plane on the a axis with the carbon atom of CO_2
REVC(N)	Repulsive energy of all carbon atoms in the Nth plane on the a axis with the carbon atom of CO_2
ETOTC	Total attractive energy for the carbon atom of CO_2
RETOTC	Total repulsive energy for the carbon atom of CO_2
ETOT	Total attractive energy for the CO_2 molecule
RETOT	Total repulsive energy for the CO_2 molecule
EFIN	Total interaction energy for the CO_2 molecule

5. CO_2 ON ANISOTROPIC GRAPHITE, ADSORBED PERPENDICULAR TO THE BASAL PLANE

The expression to be summed is

$$-T/R^6[(2-6r^2/R^2) + (9r^2/R^4)(r^2+Uz^2)] + F/R^{12}.$$

The summation logic is the same as that for the inert gas adsorbed above the center of a hexagon, with the modification that three distances to the basal plane (one for each atom of the CO_2 molecule) must be used simultaneously. The expression for the energy of attraction is of course replaced by the above expression.

Definitions of Symbols in the Program

T	Attractive Constant
F	Repulsive Constant
Q	Upper limit to the distance of the carbon atom of CO_2 from the surface
U	Ratio of the parallel to the perpendicular component of polarizability for CO_2
NN	Upper limit to N
K	Upper limit to J
M	Upper limit to I

The appendages C, N, and F to variables refer to center, near, and far atoms of the CO_2 molecule relative to the surface. In other respects the symbols are those used for the program pertaining to the inert gases above the center of a hexagon in the basal plane.

6. CO_2 ON ANISOTROPIC GRAPHITE, ADSORBED PARALLEL TO THE EDGE PLANE AND PARALLEL TO THE BASAL PLANES

The expression to be summed is

$$-T/R^6[1 + U + 3z^2/R^2 - 6Ur^2 \cos^2\theta/R^2 + 9r^2 \cos^2\theta(r^2 \sin^2\theta + U)(z^2 + r^2 \cos^2\theta)/R^4] + F/R^{12}$$

where the symbols have been defined above. The transformation to a rectangular coordinate system is again made for ease in performing the summation.

The logic is similar to that used in the inert gas-edge plane case, program 3 above. Letting one of the carbon atoms which juts out from the surface be the origin of a rectangular coordinate system, the coordinates of the carbon atoms of the graphite lattice relative to an adatom at (X, Y) may be listed as functions of N, I, and J, where

N refers to the number of the plane as we move into the bulk crystal,

I refers to the subscript variable corresponding to the b axis,

J refers to the subscript variable corresponding to the a axis.

For example, when

N = 1, 3, 5, ...

B(N, I) = IB − X for carbon atoms in the positive b direction

B(N, I) = IB + X for carbon atoms in the negative b direction,

when

N = 1, 4, 7, 10, ...

A(N, J) = 2JA − Y for carbon atoms in the positive a direction

A(N, J) = 2(J − 1)A + Y for carbon atoms in the negative a direction,

and so on. Summation over all (N, I, J) atoms for the appropriate expressions covers all the carbon atoms of the crystal up to the desired limits.

Definitions of Symbols in the Program

In general, the following notation is used: the final C indicates the carbon atom of CO_2; the final E indicates the oxygen atom on CO_2; an R or L preceding the above indicates the positive or negative b direction; U or D preceding the C or E indicates the positive or negative a direction.

The number 2 inserted between the above symbols indicates the same quantity as in its absence, only squared.

T	Attractive Constant
F	Repulsive Constant
XC	Displacement of the carbon atom of CO_2 from the a axis in the b direction
YC	Displacement of the carbon atom of CO_2 from the b axis in the a direction
Z	Distance of the molecule from surface
D	Distance between successive edge planes
B	Unit of distance in the b direction
A	Unit of distance in the a direction
NN	Upper limit to N
M	Upper limit to I
K	Upper limit to J
Q	Upper limit to Z
U	Ratio of parallel to perpendicular components of polarizability of CO_2

Only the symbol for the cases of C, R, and U will be explicitly defined in this list.

LBRC(N, I)	Distance along the b axis in the positive direction to the Ith location in the Nth plane
LAUC(N, J)	Distance along the a axis in the positive direction to the Jth location in the Nth plane
F2(N)	Distance squared from the molecule to the Nth plane
RUR2C(N, I, J)	Distance squared from the carbon atom of CO_2 to the (N, I, J) th carbon atom in the "upper-right" quadrant of the coordinate system
REIC(N, I, J)	Total repulsive energy of the carbon atom in CO_2
EURC(N, I, J)	Attractive energy of the carbon atom in CO_2 and carbon atoms in the "upper-right" quadrant of the coordinate system
EC(N)	Attractive energy of the carbon atom in CO_2 up to the Nth plane
REC(N)	Repulsive energy of the carbon atom in CO_2 up to the Nth plane
ED(N)	Total interaction energy of the Nth plane
ETOTC	Total attractive energy of the carbon atom in CO_2
RETOTC	Total repulsive energy of the carbon atom in CO_2

ETOT	Total attractive energy
RETOT	Total repulsive energy
EFIN	Total interaction energy

7. CO_2 ON ANISOTROPIC GRAPHITE, ADSORBED PARALLEL TO THE EDGE PLANE AND PERPENDICULAR TO THE BASAL PLANES

The expression to be summed is

$$-T/R^6[2-6(z^2+r^2\cos^2\theta)/R^2+9(z^2+r^2\cos^2\theta)(z^2+r^2\cos^2\theta+U\cdot r^2\sin^2\theta)/R^4]+F/R^{12}$$

where the symbols have been defined above. There is no essential difference between the logic and definitions of this program and the previous one.

8. CO_2 ON ANISOTROPIC GRAPHITE, ADSORBED PERPENDICULAR TO THE EDGE PLANE

The expression to be summed is

$$-T/R^6[1+U-6(r^2\cos^2\theta+U\cdot z^2)/R^2+9(z^2+r^2\cos^2\theta)(r^2+U\cdot z^2)/R^4]+F/R^{12}$$

where the symbols have been defined above. A rectangular coordinate system is again used, in place of the cylindrical one arising from the derivation of the equation, for convenience in summing. The logic here is based on that immediately preceding, with the modification that three distances (one for each atom of CO_2) must be considered simultaneously.

Definitions of Symbols in the Program

Since the position of each atom of CO_2 is the same relative to the a and b directions, the added C and E to distinguish between carbon and oxygen is no longer necessary. Symbols which have been defined in the previous edge programs will not be redefined here.

ZC	Distance of center atom of CO_2 from the surface
ZN	Distance of near atom of CO_2 from the surface
ZF	Distance of far atom of CO_2 from the surface

Other notation introduces nothing new.

The programs for adsorption of CO_2 with an assumed isotropic polarizability are produced readily from the above by substituting U = 1, and the appropriate attractive and repulsive constants. The latter are obtained by repeating the evaluation of these constants with the assumption of an isotropic CO_2 molecule.

In the case of an isotropic graphite, however, the situation is more complex. New expressions for the dispersion interaction must be substituted for the "attractive energy" portions of the programs. The appropriate constants must also be evaluated. For the following programs we simply indicate the expressions to be summed, since the logic and definitions do not change from the corresponding ones for anisotropic graphite.

When graphite is assumed isotropic, the distinction between the energy expressions for the basal and edge planes disappears. Therefore, the following two programs suffice for all cases considered on isotropic graphite.

9. CO_2 ON ISOTROPIC GRAPHITE, ADSORBED PARALLEL TO SURFACE

The expression to be summed is

$$-T/R^6 \left\{ 2 + U - 6[z^2 + r^2(\cos^2\theta + U \cdot \sin^2\theta)]/R^2 + 9z^2r^2(\cos^2\theta + U \cdot \sin^2\theta)/ \right.$$

$$\left. R^4 + 9z^2/R^2 + 9r^4[\sin^2\theta \cos^2\theta(1 + U) + \cos^4\theta + U \cdot \sin^4\theta]/R^4 \right\} + F/R^{12}.$$

(It must be pointed out explicitly that there is a slight inconsistency in our definition of the relationship between the cylindrical and rectangular coordinate systems. For the case of CO_2 parallel to the basal plane, $a = r \sin\theta$ and $b = r \cos\theta$; the converse of all other cases.)

10. CO_2 ON ISOTROPIC GRAPHITE, ADSORBED PERPENDICULAR TO SURFACE

The expression to be summed is

$$-T/R^6[2 + U - 6(r^2 + U \cdot z^2)/R^2 + 9z^2r^2(1 + U)/R^4 + 9(r^4 + U \cdot z^4)/R^4] + F/R^{12}$$

The final calculation involves the assumption of both isotropic CO_2 and isotropic graphite. This situation is readily disposed of by making U equal to unity in the above expressions, and substituting the appropriate values of the attractive and repulsive constants.

PROGRAM 1

```
      PROGRAM GRAPHITE
  100 FORMAT(25H  BASAL PLANE, HEX, XENON///
     110H  ALPHA = E11.3/
     510H  B     = E11.3/
     610H  RHO   = F6.3///)
  102 FORMAT(28H   N     E(N,1)        RE(N,1)/)
  103 FORMAT(2X,I2,2E13.5)
  104 FORMAT(//26H   J     E(J)         RE(J)/)
  105 FORMAT(//17H  E ATTRACTION = E13.5/)
  106 FORMAT(17H  E REPULSION  = E13.5/)
  107 FORMAT(17H  E TOTAL(CALS)= E13.5)
  108 FORMAT(7H   Z = F6.3///)
      DIMENSION Q(10,10),
     1Y(10,10,10), R(10,10), S(10,10),
     2RR(10,10), Z(10),
     3T(10,10,10), EP2(10), EP(10,10), E(10,10,10),
     4RE(10,10,10),REP(10,10),REP2(10)
      ALPHA =5.72E+5
      B=45.8E+8
      RHO=-3.25
      DO 1 N=1,10,1
      DO 1 I=1,N,1
    1 Q(N,I)=12
      DO 2 N=1,10,1
    2 Q(N,1)=6
      DO 3 J=1,10,1
    3 Z(J)=3.20+(J-1)*3.35
    4 DO 5 N=1,10,1
    5 S(N,1)=((3.0/2.0)*N-(3.0/4.0)-((-1.0)**N)/4.0)
      DO 6 N=1,10,1
      DO 6 I=1,N,1
      RR(N,I)=(S(N,1)+((-1)**N+(-1)**(N+I))/4.0)**2+(0.75)*((I-1)**2)
    6 R(N,I)=(SQRTF(RR(N,I)))*1.42
      DO 7 N=1,10,1
      DO 7 I=1,N,1
      DO 7 J=1,10,1
      Y(N,I,J)=SQRTF(Z(J)**2+(R(N,I))**2)
      E(N,I,J)=Q(N,I)*(2*(Y(N,I,J))**2+3*(R(N,I))**2)/(Y(N,I,J)**8)
    7 RE(N,I,J)=(Q(N,I)*B)/(Y(N,I,J)**12)
      ETOT=0.0
      RETOT=0.0
      DO 8 N=1,10,1
      EP(N,1)=0.0
      REP(N,1)=0.0
      DO 8 I=1,N,1
      EP(N,1)=EP(N,1)+E(N,I,1)
    8 REP(N,1)=REP(N,1)+RE(N,I,1)
      DO 10 J=1,10,1
      EP2(J)=0.0
      REP2(J)=0.0
      DO 9 N=1,10,1
      DO 9 I=1,N,1
      EP2(J)=EP2(J)+E(N,I,J)
    9 REP2(J)=REP2(J)+RE(N,I,J)
      ETOT=ETOT+EP2(J)
   10 RETOT=RETOT+REP2(J)
```

```
      ETOT=ETOT*ALPHA
      EFIN=RETOT-ETOT
      PRINT 102,
      DO 200 N=1,10,1
  200 PRINT 103, N,EP(N,1),REP(N,1)
      PRINT 104,
      DO 201 J=1,10,1
  201 PRINT 103, J,EP2(J),REP2(J)
      PRINT 105, ETOT
      PRINT 106, RETOT
      PRINT 107, EFIN
      PRINT 108, Z(1)
      DO 11 J=1,10,1
   11 Z(J)=Z(J)+0.10
      IF(Z(1)-4.0)4,12,12
   12 PRINT 100, ALPHA,B,RHO
      END
```

PROGRAM 2

```
      PROGRAM GRAPHITE
100 FORMAT(27H  BASAL PLANE, C ATOM, NEON///
   110H  ALPHA = E11.3/
   510H  B     = E11.3/)
102 FORMAT(54H   N  ETOTP(N,1)   ETOTQ(N,1)  RETOTP(N,1) RETOTQ(N,1)/)
103 FORMAT(2X,I2,4E13.5)
104 FORMAT(//27H   J   ETOTJ(J)   RETOTJ(J)/)
105 FORMAT(2X,I2,2E13.5)
106 FORMAT(30H  ENERGIES (CAL/MOLE) FOR Z = F6.2/
   119H       ATTRACTION = E13.5/
   219H       REPULSION  = E13.5/
   319H       TOTAL      = E13.5)
    DIMENSION DP0(10), DQ0(10), SP(10), SQ(10), YP0(10,10), P(10,27),
   1TP0(10,10), EP0(10,10), YQ0(10,10), TQ0(10,10), EQ0(10,10),
   2DP(10,27), DQ(10,29), YP(10,27,10), TP(10,27,10),  Z(10),
   3EP(10,27,10), YQ(10,29,10), TQ(10,29,10), EQ(10,29,10), Q(10,29),
   4EPT(10,10), ETOTP(10,10), EQT(10,10), ETOTQ(10,10), ETOTJ(10),
   5REP0(10,10),REQ0(10,10),REP(10,27,10),REQ(10,29,10),REPT(10,10),
   6RETOTP(10,10),REQT(10,10),RETOTQ(10,10),RETOTJ(10),RRR(10),
   7EEE(10)
    TYPE INTEGER DP0, DQ0, SP, SQ
    ALPHA = 0.558E+5
    B=1.50E+8
    DO 20 J=1,10,1
 20 Z(J)=3.00+(J-1)*3.35
    DO 1 N=1,10,1
    DP0(N)=(3*N-2)
    DQ0(N)=(3*N)
    SP(N)=3*N-3
  1 SQ(N)=3*N-1
 13 DO 2 N=1,10,1
    DO 2 J=1,10,1
    YP0(N,J)=SQRTF(Z(J)**2+(DP0(N)*1.42)**2)
    EP0(N,J)=(3.0*(2*(YP0(N,J))**2+3*((DP0(N)*1.42)**2)))/(YP0(N,J)*
   1 *8)
    REP0(N,J)=3*B/(YP0(N,J)**12)
    YQ0(N,J)=SQRTF(Z(J)**2+(DQ0(N)*1.42)**2)
    REQ0(N,J)=3*B/(YQ0(N,J)**12)
  2 EQ0(N,J)=(3.0*(2*(YQ0(N,J))**2+3*((DQ0(N)*1.42)**2)))/(YQ0(N,J)*
   1 *8)
    DO 21 N=1,10,1
    K=SP(N)
    DO 21 I=1,K,1
 21 P(N,I)=DP0(N)**2-3*I*DP0(N)+3*I**2
    DO 3 N=1,10,1
    K=SP(N)
    DO 3 I=1,K,1
  3 DP(N,I)=(SQRTF(P(N,I)))*1.42
    DO 22 N=1,10,1
    L=SQ(N)
    DO 22 I=1,L,1
 22 Q(N,I)=DQ0(N)**2-3*I*DQ0(N)+3*I**2
    DO 4 N=1,10,1
    L=SQ(N)
    DO 4 I=1,L,1
  4 DQ(N,I)=(SQRTF(Q(N,I)))*1.42
```

```
      DO 5 N=1,10,1
      M=SP(N)
      DO 5 I=1,M,1
      DO 5 J=1,10,1
      YP(N,I,J)=SQRTF(Z(J)**2+DP(N,I)**2)
      REP(N,I,J)=3*B/(YP(N,I,J)**12)
    5 EP(N,I,J)=(3.0*(2*(YP(N,I,J))**2+3*(DP(N,I))**2))/(YP(N,I,J)**8)
      DO 6 N=1,10,1
      KK=SQ(N)
      DO 6 I=1,KK,1
      DO 6 J=1,10,1
      YQ(N,I,J)=SQRTF(Z(J)**2+DQ(N,I)**2)
      REQ(N,I,J)=3*B/(YQ(N,I,J)**12)
    6 EQ(N,I,J)=(3.0*(2*(YQ(N,I,J))**2+3*(DQ(N,I))**2))/(YQ(N,I,J)**8)
      DO 7 N=1,10,1
      DO 7 J=1,10,1
      EPT(N,J)=0.0
      REPT(N,J)=0.0
      LL=SP(N)
      DO 7 I=1,LL,1
      REPT(N,J)=REPT(N,J)+REP(N,I,J)
    7 EPT(N,J)=EPT(N,J)+EP(N,I,J)
      DO 8 N=1,10,1
      DO 8 J=1,10,1
      RETOTP(N,J)=0.0
      ETOTP(N,J)=0.0
      RETOTP(N,J)=REP0(N,J)+REPT(N,J)
    8 ETOTP(N,J)=EP0(N,J)+EPT(N,J)
      DO 9 N=1,10,1
      DO 9 J=1,10,1
      REQT(N,J)=0.0
      EQT(N,J)=0.0
      MM=SQ(N)
      DO 9 I=1,MM,1
      REQT(N,J)=REQT(N,J)+REQ(N,I,J)
    9 EQT(N,J)=EQT(N,J)+EQ(N,I,J)
      DO 10 N=1,10,1
      DO 10 J=1,10,1
      RETOTQ(N,J)=0.0
      ETOTQ(N,J)=0.0
      RETOTQ(N,J)=REQ0(N,J)  +REQT(N,J)
   10 ETOTQ(N,J)=EQ0(N,J)+EQT(N,J)
      RETOT=0.0
      ETOT=0.0
      DO 12 J=1,10,1
      RETOTJ(J)=0.0
      ETOTJ(J)=0.0
      RRR(J)=B/(Z(J)**12)
      EEE(J)=2.0/(Z(J)**6)
      DO 11 N=1,10,1
      RETOTJ(J)=RETOTJ(J)+RETOTP(N,J)+RETOTQ(N,J)
   11 ETOTJ(J)=ETOTJ(J)+ETOTP(N,J)+ETOTQ(N,J)
      RETOT=RETOT+RETOTJ(J)+RRR(J)
   12 ETOT=ETOT+ETOTJ(J)+EEE(J)
      ETOT=ETOT*ALPHA
      PRINT 102,
```

```
    DO 200 N=1,10,1
200 PRINT 103,N,ETOTP(N,1),ETOTQ(N,1),RETOTP(N,1),RETOTQ(N,1)
    PRINT 104,
    DO 201 J=1,10,1
201 PRINT 105,J,ETOTJ(J),RETOTJ(J)
    EFIN=RETOT-ETOT
    PRINT 106, Z(1), ETOT, RETOT, EFIN
    DO 14 J=1,10,1
 14 Z(J)=Z(J)+0.10
    IF(Z(1)-3.2)13,15,15
 15 PRINT 100, ALPHA,B
    END
```

PROGRAM 3

```
      PROGRAM GRAPHITE
100 FORMAT(32H  GRAPHITE  EDGE ATOMS, KRYPTON///
   110H  ALPHA = E11.3/
   510H  A     = F6.3/
   610H  B     = F6.3/
   710H  C     = F6.3/
   810H  D     = F6.3/
   910H  V     = F6.3/
   110H  BB    = E11.3/
   210H  RHO   = F6.3///)
101 FORMAT(44H DISPL OF ADATOM FROM EDGE OF BASAL PLANE = F6.3/)
102 FORMAT(//15H  ATTRACTION = E13.5//
   115H REPULSION  = E13.5//
   228H  TOTAL INTERACTION FOR Z = F6.3/
   39H        = E13.5//)
103 FORMAT(//20H  ATTRACTION(GAP) = E13.5//
   120H   REPULSION(GAP) = E13.5//
   233H  TOTAL INTERACTION(GAP) FOR Z = F6.3/
   39H        = E13.5//)
104 FORMAT(//45H ENERGY AS FN(DEPTH), N      C ATOM         GAP/)
105 FORMAT(21X, I2, 2E13.5)
      DIMENSION Q(30,9,7), QP(30,9,7),
   1LA(30,7), LAP(30,7),
   2LB(30,9), LBP(30,9),
   3          LEP(30,7),
   4E(30), EP(30), F(30), FP(30),
   5ET(30,9,7), ETP(30,9,7), ETP2(30,9,7),
   6LR(30,9), LRP(30,9), LRP2(30,9),EDP(10),ED(10)
   7R(30,9,7), RP(30,9,7), RP2(30,9,7)
   8T(30,9,7), TP(30,9,7), TP2(30,9,7)
   9RET(30,9,7),RETP(30,9,7),RETP2(30,9,7),RE(30),REP(30)
      TYPE REAL LA,LAP,LB,LBP,LEP,LR,LRP,LRP2
      ALPHA=3.52E+5
      A=3.35
      B=2.459
      C=1.230
      D=0.71
      BB = 20.2E+8
      RHO =-3.30
      V=3.35
      K = 7
      NN = 30
      M = 9
      X=2.472
      Y=3.400
      ZP=1.8
      Z=2.9
      DO 1 N=1,NN,2
      DO 1 I=1,M,1
      LB(N,I) = (I-1)*B
    1 LBP(N,I) = (I-1)*B
      DO 2 N=2,NN,2
      DO 2 I=1,M,1
      LB(N,I) = C+(I-1)*B
    2 LBP(N,I) = C+(I-1)*B
      DO 3 N=1,NN,3
```

```
      DO 3 J=1,K,1
      LA(N,J) = 2*(J-1)*A
      LAP(N,J) = X+2*(J-1)*A
    3 LEP(N,J) = 2*V-X+2*(J-1)*A
      DO 4 N=2,NN,3
      DO 4 J=1,K,1
      LA(N,J) = (J-1)*A
      LAP(N,J) = X+(J-1)*A
    4 LEP(N,J) = V-X+(J-1)*A
      DO 5 N=3,NN,3
      DO 5 J=1,K,1
      LA(N,J) = (2*J-1)*A
      LAP(N,J) = V+X+2*(J-1)*A
    5 LEP(N,J) = V-X+2*(J-1)*A
      DO 6 N=1,NN,1
      DO 6 I=1,M,1
      DO 6 J=1,K,1
    6 QP(N,I,J) = 2
      DO 7 N=1,NN,2
      DO 7 J=1,K,1
    7 QP(N,1,J) = 1
      DO 8 N=1,NN,1
      DO 8 I=1,M,1
      DO 8 J=1,K,1
    8 Q(N,I,J) = 4
      DO 9 N=1,NN,6
    9 Q(N,1,1) = 1
      DO 10 N=5,NN,6
   10 Q(N,1,1) = 1
      DO 11 N=1,NN,6
      DO 11 J=2,K,1
   11 Q(N,1,J) = 2
      DO 12 N=5,NN,6
      DO 12 J=2,K,1
   12 Q(N,1,J) = 2
      DO 13 N=1,NN,6
      DO 13 I=2,M,1
   13 Q(N,I,1) = 2
      DO 14 N=5,NN,6
      DO 14 I=2,M,6
   14 Q(N,I,1) = 2
      DO 15 N=2,NN,6
      DO 15 I=1,M,1
   15 Q(N,I,1) = 2
      DO 16 N=4,NN,6
      DO 16 I=1,M,1
   16 Q(N,I,1) = 2
      DO 17 N=3,NN,6
      DO 17 J=1,K,1
   17 Q(N,1,J) = 2
   23 Z=Z+0.10
      ZP=ZP+0.10
      DO 20 N=1,NN,1
      F(N) = (Z+(N-1)*D)**2
   20 FP(N) = (ZP+(N-1)*D)**2
      DO 21 N=1,NN,1
```

```
      DO 21 I=1,M,1
      LR(N,I) = SQRTF(F(N)+LB(N,I)**2)
      LRP(N,I) = SQRTF(FP(N)+LBP(N,I)**2)
   21 LRP2(N,I) = LRP(N,I)
      DO 22 N=1,NN,1
      DO 22 I=1,M,1
      DO 22 J=1,K,1
      R(N,I,J) = SQRTF(F(N)+LB(N,I)**2+LA(N,J)**2)
      RP(N,I,J) = SQRTF(FP(N)+LBP(N,I)**2+LAP(N,J)**2)
      RP2(N,I,J) = SQRTF(FP(N)+LBP(N,I)**2+LEP(N,J)**2)
      ET(N,I,J) = (Q(N,I,J)*(2*(R(N,I,J))**2+3*(LR(N,I))**2))/(R(N,I,
     1 J)**8)
      RET(N,I,J)=(Q(N,I,J)*BB)/(R(N,I,J)**12)
      ETP(N,I,J) =(QP(N,I,J)*(2*(RP(N,I,J))**2+3*(LRP(N,I))**2))/(RP
     1 (N,I,J)**8)
      RETP(N,I,J)=(QP(N,I,J)*BB)/(RP(N,I,J)**12)
      RETP2(N,I,J)=(QP(N,I,J)*BB)/(RP2(N,I,J)**12)
   22 ETP2(N,I,J) =(QP(N,I,J)*(2*(RP2(N,I,J))**2+3*(LRP2(N,I))**2))/(
     1 RP2(N,I,J)**8)
      ETOT = 0.0
      RETOT=0.0
      ETOTP = 0.0
      RETOTP=0.0
      DO 31 N=1,NN,1
      E(N)=0.0
      RE(N)=0.0
      EP(N)=0.0
      REP(N)=0.0
      DO 30 I=1,M,1
      DO 30 J=1,K,1
      E(N) = E(N) + ET(N,I,J)
      RE(N)=RE(N)+RET(N,I,J)
      REP(N)=REP(N)+RETP(N,I,J)+RETP2(N,I,J)
   30 EP(N) = EP(N) + ETP(N,I,J) + ETP2(N,I,J)
      ETOT = ETOT + E(N)
      RETOT=RETOT+RE(N)
      RETOTP=RETOTP+REP(N)
   31 ETOTP = ETOTP + EP(N)
      ETOT=ETOT*ALPHA
      ETOTP=ETOTP*ALPHA
      EFIN=0.0
      EPFIN=0.0
      EFIN=EFIN+RETOT-ETOT
      EPFIN=EPFIN+RETOTP-ETOTP
      PRINT 102, ETOT, RETOT, Z, EFIN
      PRINT 103, ETOTP, RETOTP, ZP, EPFIN
      PRINT 104,
      DO 50 N=1,10,1
      EDP(N)=REP(N)-EP(N)*ALPHA
      ED(N)=RE(N)-E(N)*ALPHA
   50 PRINT 105, N, ED(N), EDP(N)
      IF(Z-3.8)23,24,24
   24 PRINT 100, ALPHA,A,B,C,D,V,BB,RHO
      PRINT 101, X
      END
```

PROGRAM 4

```
      PROGRAM GRAPHITE
C     LINEAR ADATOM PARALLEL TO BASAL PLANE - CO2 ON GRAPHITE
  102 FORMAT(//15H  ATTRACTION = E13.5//
     115H  REPULSION  = E13.5/
     228H  TOTAL INTERACTION FOR Z = F6.3/
     39H        = E13.5//)
  103 FORMAT(//34H ENERGY AS FN(DEPTH), N      ENERGY/)
  104 FORMAT(21X,I2,E13.5)
      COMMON/B/ LBG2C(10),LBG2E(10),LBP2C(10),LBP2E(10),LBR2C(10),LBR2
     1E(10),LBB2C(10),LBB2E(10),LAG2C(10),LAG2E(10),LAP2C(10),LAP2E(10
     2),LAR2C(10),LAR2E(10),LAB2C(10),LAB2E(10),F2(10),RGC2(10,10,10),
     3RGE2(10,10,10),RPC2(10,10,10),RPE2(10,10,10),RRC2(10,10,10),
     4RRE2(10,10,10),RBC2(10,10,10),RBE2(10,10,10),REIC(10,10,10),
     5REIE(10,10,10),EGC(10,10,10),EGE(10,10,10),EPC(10,10,10),
     6EPE(10,10,10),ERC(10,10,10),ERE(10,10,10),EBC(10,10,10)
      COMMON/A/ EBE(10,10,10),LAVPC2(10),LAVRC2(10),RVPC2(10,10),
     1RVPE2(10,10),RVRC2(10,10),RVRE2(10,10),EVPC(10,10),
     2EVRC(10,10),EVPE(10,10),EVRE(10,10),EC(10),EE(10),E(10),
     3REC(10),REE(10),RE(10),EVC(10),EVE(10),REVC(10),REVE(10),
     4REIVC(10,10),REIVE(10,10),ED(10),LBG2EP(10),LBP2EP(10),LBR2EP(10),
     5LBB2EP(10),RGE2P(10,10,10),RPE2P(10,10,10),RRE2P(10,10,10),RBE2P(1
     60,10,10)
      TYPE REAL LBG2C,LBG2E,LBP2C,LPB2E,LBR2C,LBR2E,LBB2C,LBB2E,
     1LAG2C,LAG2E,LAP2C,LAP2E,LAR2C,LAR2E,LAB2C,LAB2E,LAVPC2,
     2LAVRC2,LBG2EP,LBP2EP,LBB2EP
      BANK,(0),/A/
      T=2.79E+5
      F=1.56E+9
      XC=0
      YC=0
      XE=1.16
      XEP=-1.16
      YE=0
      Z=3.2
      D=3.35
      A=4.26
      B=2.459
      NN=10
      K=10
      M=10
      Q=3.6
      U=2.08
      C=0.71
      DO 1 I=1,M,1
      LBG2C(I)=(0.5*B-XC+(I-1)*B)**2
      LBG2E(I)=(0.5*B-XE+(I-1)*B)**2
      LBG2EP(I)=(0.5*B-XEP+(I-1)*B)**2
      LBP2C(I)=(B-XC+(I-1)*B)**2
      LBP2E(I)=(B-XE+(I-1)*B)**2
      LBP2EP(I)=(B-XEP+(I-1)*B)**2
      LBR2C(I)=LBP2C(I)
      LBR2E(I)=LBP2E(I)
      LBR2EP(I)=LBP2EP(I)
      LBB2C(I)=LBG2C(I)
      LBB2E(I)=LBG2E(I)
    1 LBB2EP(I)=LBG2EP(I)
      DO 2 J=1,K,1
      LAG2C(J)=(C-YC+(J-1)*A)**2
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      LAG2E(J)=(C-YE+(J-1)*A)**2
      LAP2C(J)=(2.0*C-YC+(J-1)*A)**2
      LAP2E(J)=(2.0*C-YE+(J-1)*A)**2
      LAR2C(J)=(4.0*C-YC+(J-1)*A)**2
      LAR2E(J)=(4.0*C-YE+(J-1)*A)**2
      LAB2C(J)=(5.0*C-YC+(J-1)*A)**2
      LAB2E(J)=(5.0*C-YE+(J-1)*A)**2
      LAVPC2(J)=(1.42+(J-1)*A)**2
    2 LAVRC2(J)=(2.84+(J-1)*A)**2
   25 Z=Z+0.10
      DO 3 N=1,NN,1
    3 F2(N)=(Z+(N-1)*D)**2
      DO 4 N=1,NN,1
      DO 4 I=1,M,1
      DO 4 J=1,K,1
      RGC2(N,I,J)=F2(N)+LBG2C(I)+LAG2C(J)
      RGE2(N,I,J)=F2(N)+LBG2E(I)+LAG2E(J)
      RGE2P(N,I,J)=F2(N)+LBG2EP(I)+LAG2E(J)
      RPC2(N,I,J)=F2(N)+LBP2C(I)+LAP2C(J)
      RPE2(N,I,J)=F2(N)+LBP2E(I)+LAP2E(J)
      RPE2P(N,I,J)=F2(N)+LBP2EP(I)+LAP2E(J)
      RRC2(N,I,J)=F2(N)+LBR2C(I)+LAR2C(J)
      RRE2(N,I,J)=F2(N)+LBR2E(I)+LAR2E(J)
      RRE2P(N,I,J)=F2(N)+LBR2EP(I)+LAR2E(J)
      RBC2(N,I,J)=F2(N)+LBB2C(I)+LAB2C(J)
      RBE2(N,I,J)=F2(N)+LBB2E(I)+LAB2E(J)
      RBE2P(N,I,J)=F2(N)+LBB2EP(I)+LAB2E(J)
      REIC(N,I,J)=F/(RGC2(N,I,J)**6)+F/(RPC2(N,I,J)**6)+F/(RRC2(N,I,J)
     1**6)+F/(RBC2(N,I,J)**6)
      REIE(N,I,J)=F/(RGE2(N,I,J)**6)+F/(RPE2(N,I,J)**6)+F/(RRE2(N,I,J)
     1**6)+F/(RBE2(N,I,J)**6)+F/RGE2P(N,I,J)**6+F/RPE2P(N,I,J)**6+F/RRE2
     2P(N,I,J)**6+F/RBE2P(N,I,J)**6
      EGC(N,I,J)=(T/(RGC2(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBG2C(I)+LAG2
     1C(J)))/(RGC2(N,I,J)**2)+(1.0/RGC2(N,I,J))*((9.0*(LBG2C(I)+LAG2C(
     2J)))/RGC2(N,I,J)-6.0)*(LBG2C(I)+U*LAG2C(J)))
      EGE(N,I,J)=(T/(RGE2(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBG2E(I)+LAG2
     1E(J)))/(RGE2(N,I,J)**2)+(1.0/RGE2(N,I,J))*((9.0*(LBG2E(I)+LAG2E(
     2J)))/RGE2(N,I,J)-6.0)*(LBG2E(I)+U*LAG2E(J)))
     3+(T/(RGE2P(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBG2EP(I)+LAG2E(J)))/(RG
     4E2P(N,I,J)**2)+(1.0/RGE2P(N,I,J))*((9.0*(LBG2EP(I)+LAG2E(J)))/RGE2
     5P(N,I,J)-6.0)*(LBG2EP(I)+U*LAG2E(J)))
      EPC(N,I,J)=(T/(RPC2(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBP2C(I)+LAP2
     1C(J)))/(RPC2(N,I,J)**2)+(1.0/RPC2(N,I,J))*((9.0*(LBP2C(I)+LAP2C(
     2J)))/RPC2(N,I,J)-6.0)*(LBP2C(I)+U*LAP2C(J)))
      EPE(N,I,J)=(T/(RPE2(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBP2E(I)+LAP2
     1E(J)))/(RPE2(N,I,J)**2)+(1.0/RPE2(N,I,J))*((9.0*(LBP2E(I)+LAP2E(
     2J)))/RPE2(N,I,J)-6.0)*(LBP2E(I)+U*LAP2E(J)))
     3+(T/(RPE2P(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBP2EP(I)+LAP2E(J)))/(RP
     4E2P(N,I,J)**2)+(1.0/RPE2P(N,I,J))*((9.0*(LBP2EP(I)+LAP2E(J)))/RPE2
     5P(N,I,J)-6.0)*(LBP2EP(I)+U*LAP2E(J)))
      ERC(N,I,J)=(T/(RRC2(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBR2C(I)+LAR2
     1C(J)))/(RRC2(N,I,J)**2)+(1.0/RRC2(N,I,J))*((9.0*(LBR2C(I)+LAR2C(
     2J)))/RRC2(N,I,J)-6.0)*(LBR2C(I)+U*LAR2C(J)))
      ERE(N,I,J)=(T/(RRE2(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBR2E(I)+LAR2
     1E(J)))/(RRE2(N,I,J)**2)+(1.0/RRE2(N,I,J))*((9.0*(LBR2E(I)+LAR2E(
     2J)))/RRE2(N,I,J)-6.0)*(LBR2E(I)+U*LAR2E(J)))
     3+(T/(RRE2P(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBR2EP(I)+LAR2E(J)))/(RR
     4E2P(N,I,J)**2)+(1.0/RRE2P(N,I,J))*((9.0*(LBR2EP(I)+LAR2E(J)))/RRE2
     5P(N,I,J)-6.0)*(LBR2EP(I)+U*LAR2E(J)))
      EBC(N,I,J)=(T/(RBC2(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBB2C(I)+LAB2
     1C(J)))/(RBC2(N,I,J)**2)+(1.0/RBC2(N,I,J))*((9.0*(LBB2C(I)+LAB2C(
     2J)))/RBC2(N,I,J)-6.0)*(LBB2C(I)+U*LAB2C(J)))
    4 EBE(N,I,J)=(T/(RBE2(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBB2E(I)+LAB2
     1E(J)))/(RBE2(N,I,J)**2)+(1.0/RBE2(N,I,J))*((9.0*(LBB2E(I)+LAB2E(
     2J)))/RBE2(N,I,J)-6.0)*(LBB2E(I)+U*LAB2E(J)))
     3+(T/(RBE2P(N,I,J)**3))*(1.0+U+(9.0*F2(N)*(LBB2EP(I)+LAB2E(J)))/(RB
     4E2P(N,I,J)**2)+(1.0/RBE2P(N,I,J))*((9.0*(LBB2EP(I)+LAB2E(J)))/RBE2
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```
   5P(N,I,J)-6.0)*(LBB2EP(I)+U*LAB2E(J)))
    LBVE2=XE**2
    DO 6 N=1,NN,1
    DO 6 J=1,K,1
    RVPC2(N,J)=F2(N)+LAVPC2(J)
    RVPE2(N,J)=RVPC2(N,J)+LBVE2
    RVRC2(N,J)=F2(N)+LAVRC2(J)
    RVRE2(N,J)=RVRC2(N,J)+LBVE2
    EVPC(N,J)=(T/(RVPC2(N,J)**3))*(1.0+U*(9.0*F2(N)*LAVPC2(J))/(RVPC2
   1(N,J)**2)+(1.0/RVPC2(N,J))*(9.0*LAVPC2(J)/RVPC2(N,J)-6.0)*U*LAVPC
   22(J))
    EVRC(N,J)=(T/(RVRC2(N,J)**3))*(1.0+U*(9.0*F2(N)*LAVRC2(J))/(RVRC2
   1(N,J)**2)+(1.0/RVRC2(N,J))*(9.0*LAVRC2(J)/RVRC2(N,J)-6.0)*U*LAVRC
   22(J))
    EVPE(N,J)=(T/(RVPE2(N,J)**3))*(1.0+U*(9.0*F2(N)*(LBVE2+LAVPC2(J))
   1)/(RVPE2(N,J)**2)+(1.0/RVPE2(N,J))*(9.0*LAVPC2(J)/RVPE2(N,J)-6.0)
   2*U*LAVPC2(J))
    EVRE(N,J)=(T/(RVRE2(N,J)**3))*(1.0+U*(9.0*F2(N)*(LBVE2+LAVRC2(J))
   1)/(RVRE2(N,J)**2)+(1.0/RVRE2(N,J))*(9.0*LAVRC2(J)/RVRE2(N,J)-6.0)
   2*U*LAVRC2(J))
    REIVC(N,J)=F/(RVPC2(N,J)**6)+F/(RVRC2(N,J)**6)
  6 REIVE(N,J)=F/(RVPE2(N,J)**6)+F/(RVRE2(N,J)**6)
    ETOTE=0.0
    ETOTC=0.0
    ETOT=0.0
    RETOTE=0.0
    RETOTC=0.0
    RETOT=0.0
    DO 9 N=1,NN,1
    EC(N)=0.0
    EE(N)=0.0
    E(N)=0.0
    REC(N)=0.0
    REE(N)=0.0
    RE(N)=0.0
    EVC(N)=0.0
    EVE(N)=0.0
    REVC(N)=0.0
    REVE(N)=0.0
    DO 7 I=1,M,1
    DO 7 J=1,K,1
    EC(N)=EC(N)+4.0*(EGC(N,I,J)+EPC(N,I,J)+ERC(N,I,J)+EBC(N,I,J))
    EE(N)=EE(N)+2.0*(EGE(N,I,J)+EPE(N,I,J)+ERE(N,I,J)+EBE(N,I,J))
    REC(N)=REC(N)+4.0*REIC(N,I,J)
  7 REE(N)=REE(N)+2.0*REIE(N,I,J)
    DO 8 J=1,K,1
    EVC(N)=EVC(N)+(EVPC(N,J)+EVRC(N,J))*2.0
    EVE(N)=EVE(N)+(EVPE(N,J)+EVRE(N,J))*2.0
    REVC(N)=REVC(N)+2.0*REIVC(N,J)
  8 REVE(N)=REVE(N)+2.0*REIVE(N,J)
    ETOTC=ETOTC+EC(N)+EVC(N)
    RETOTC=RETOTC+REC(N)+REVC(N)
    ETOTE=ETOTE+EE(N)+EVE(N)
  9 RETOTE=RETOTE+REE(N)+REVE(N)
    EFIN=0.0
    ETOT=ETOT+ETOTC+2.0*ETOTE
    RETOT=RETOT+RETOTC+2.0*RETOTE
    EFIN=EFIN+RETOT-ETOT
    PRINT 102,ETOT,RETOT,Z,EFIN
    PRINT 103,
    DO 10 N=1,10,1
    ED(N)=REC(N)+REVC(N)-EC(N)-EVC(N)+2.0*(REE(N)+REVE(N)-EE(N)-EVE(
   1N))
 10 PRINT 104,N,ED(N)
    IF(Z-Q)25,11,11
 11 END
```

PROGRAM 5

```
      PROGRAM GRAPHITE
C     LINEAR ADATOM PERPENDICULAR TO BASAL PLANE - CO2 ON GRAPHITE
  102 FORMAT(//15H  ATTRACTION = E13.5//
     115H  REPULSION  = E13.5//
     236H  TOTAL INTERACTION FOR Z(CENTER) = F6.3/
     39H        = E13.5//)
  103 FORMAT(//34H ENERGY AS FN(DEPTH), J      ENERGY/)
  104 FORMAT(21X,I2,E13.5)
  105 FORMAT(41H N I J        YC             YN             YF)
  106 FORMAT(3I2,3E13.5)
  107 FORMAT(41H N I J        EC             EN             EF)
  108 FORMAT(41H N I J       REC            REN            REF)
      DIMENSION Q(10,10),REP(10,1),  R(10,10),S(10,10),RR(10,10),
     1ZC(10),ZN(10),ZF(10),YC(10,10,10),YN(10,10,10),YF(10,10,10),
     2EC(10,10,10),EN(10,10,10),EF(10,10,10),REF(10,10,10),REN(10,10,
     310),REC(10,10,10),EP(10,1),EP2(10),REP2(10),ED(10)
      G=4.1
      T=2.79E+5
      F=1.56E+9
      U=2.08
      NN=10
      K=10
      M=10
      DO 1 N=1,NN,1
      DO 1 I=1,N,1
    1 Q(N,I)=12
      DO 2 N=1,NN,1
    2 Q(N,1)=6
      DO 3 J=1,K,1
      ZC(J)=3.90+(J-1)*3.35
      ZN(J)=2.74+(J-1)*3.35
    3 ZF(J)=5.06+(J-1)*3.35
      DO 4 N=1,NN,1
    4 S(N,1)=((3.0/2.0)*N-(3.0/4.0)-((-1.0)**N)/4.0)
      DO 5 N=1,NN,1
      DO 5 I=1,N,1
      RR(N,I)=(S(N,1)+((-1)**N+(-1)**(N+I))/4.0)**2+(0.75)*((I-1)**2)
    5 R(N,I)=(SQRTF(RR(N,I)))*1.42
   13 DO 6 N=1,NN,1
      DO 6 I=1,N,1
      DO 6 J=1,K,1
      YC(N,I,J)=SQRTF(ZC(J)**2+(R(N,I))**2)
      YN(N,I,J)=SQRTF(ZN(J)**2+(R(N,I))**2)
      YF(N,I,J)=SQRTF(ZF(J)**2+(R(N,I))**2)
      EC(N,I,J)=Q(N,I)*(T/(YC(N,I,J)**6))*(2.0-6.0*R(N,I)**2/
     1(YC(N,I,J)**2)+(9.0*R(N,I)**2/(YC(N,I,J)**4)*(R(N,I)**2
     2+U*ZC(J)**2)))
      EN(N,I,J)=Q(N,I)*(T/(YN(N,I,J)**6))*(2.0-6.0*R(N,I)**2/
     1(YN(N,I,J)**2)+(9.0*R(N,I)**2/(YN(N,I,J)**4)*(R(N,I)**2
     2+U*ZN(J)**2)))
      EF(N,I,J)=Q(N,I)*(T/(YF(N,I,J)**6))*(2.0-6.0*R(N,I)**2/
     1(YF(N,I,J)**2)+(9.0*R(N,I)**2/(YF(N,I,J)**4)*(R(N,I)**2
     2+U*ZF(J)**2)))
      REC(N,I,J)=(Q(N,I)*F)/(YC(N,I,J)**12)
      REN(N,I,J)=(Q(N,I)*F)/(YN(N,I,J)**12)
    6 REF(N,I,J)=(Q(N,I)*F)/(YF(N,I,J)**12)
```

```
      ETOT=0.0
      RETOT=0.0
      DO 7 N=1,NN,1
      EP(N,1)=0.0
      REP(N,1)=0.0
      DO 7 I=1,N,1
      EP(N,1)=EP(N,1)+EC(N,I,1)+EN(N,I,1)+EF(N,I,1)
    7 REP(N,1)=REP(N,1)+REC(N,I,1)+REN(N,I,1)+REF(N,I,1)
      DO 9 J=1,K,1
      EP2(J)=0.0
      REP2(J)=0.0
      DO 8 N=1,NN,1
      DO 8 I=1,N,1
      EP2(J)=EP2(J)+EC(N,I,J)+EN(N,I,J)+EF(N,I,J)
    8 REP2(J)=REP2(J)+REC(N,I,J)+REN(N,I,J)+REF(N,I,J)
      ETOT=ETOT+EP2(J)
    9 RETOT=RETOT+REP2(J)
      EFIN=RETOT-ETOT
      PRINT 102,ETOT,RETOT,ZC(1),EFIN
      PRINT 103,
      DO 10 J=1,10,1
      ED(J)=REP2(J)-EP2(J)
   10 PRINT 104,J,ED(J)
      DO 14 N=1,3,2
      DO 14 I=1,N,1
      DO 14 J=1,2,1
      PRINT 105,
      PRINT 106, N,I,J,YC(N,I,J),YN(N,I,J),YF(N,I,J)
      PRINT 107,
      PRINT 106, N,I,J,EC(N,I,J),EN(N,I,J),EF(N,I,J)
      PRINT 108,
   14 PRINT 106, N,I,J,REC(N,I,J),REN(N,I,J),REF(N,I,J)
      DO 11 J=1,K,1
      ZC(J)=ZC(J)+0.10
      ZN(J)=ZN(J)+0.10
   11 ZF(J)=ZF(J)+0.10
      IF(ZC(1)-G)13,12,12
   12 END
```

PROGRAM 6

```
      PROGRAM GRAPHITE
C     LINEAR ADATOM PARALLEL ON EDGE PLANE - CO2 ON GRAPHITE
  102 FORMAT(//15H  ATTRACTION = E13.5//
     115H  REPULSION  = E13.5//
     228H  TOTAL INTERACTION FOR Z = F6.3/
     39H        = E13.5//)
  103 FORMAT(//34H ENERGY AS FN(DEPTH), N      ENERGY/)
  104 FORMAT(21X,I2,E13.5)
      COMMON/A/ LBRC(30,9),LBRE(30,9),LBLC(30,9),LBLE(30,9),LAUC(30,7),
     1LAUE(30,7),LADC(30,7),LADE(30,7),LBR2C(30,9),LBR2E(30,9),LBL2C(30
     2,9),LBL2E(30,9),LAU2C(30,7),LAU2E(30,7),LAD2C(30,7),LAD2E(30,7),
     3F2(30),RUR2C(30,9,7),RUR2E(30,9,7),RUL2C(30,9,7),RUL2E(30,9,7)
      COMMON/B/      RDR2E(30,9,7),RDL2C(30,9,7),RDL2E(30,9,7),EURC(30,9
     5,7),EURE(30,9,7),EULC(30,9,7),EULE(30,9,7),EDRC(30,9,7),EDRE(30,9
     6,7),EDLC(30,9,7),EDLE(30,9,7),F2C(30),F2E(30),E(30),RE(30),EC(30)
     7,EE(30),REC(30),REE(30),REIC(30,9,7),REIE(30,9,7),ED(30),
     8 RDR2C(30,9,7)
      TYPE REAL LBRC,LBRE,LBLC,LBLE,LAUC,LAUE,LADC,LADE,LBR2C,LBR2E,LBL
     12C,LBL2E,LAU2C,LAU2E,LAD2C,LAD2E
      BANK,(0),/A/
      T=2.79E+5
      F =1.56E+9
      XC=0.0
      XE=1.16
      YC=2.472
      YE=2.472
      Z=2.2
      D=0.71
      B=2.459
      A=3.35
      NN=30
      M=9
      K=7
      Q=2.5
      U=2.08
      DO 1 N=1,NN,2
      DO 1 I=1,M,1
      LBRC(N,I)=I*B-XC
      LBRE(N,I)=I*B-XE
      LBLC(N,I)=(I-1)*B+XC
    1 LBLE(N,I)=(I-1)*B+XE
      DO 2 N=2,NN,2
      DO 2 I=1,M,1
      LBRC(N,I)=0.5*B+(I-1)*B-XC
      LBRE(N,I)=0.5*B+(I-1)*B-XE
      LBLC(N,I)=0.5*B+(I-1)*B+XC
    2 LBLE(N,I)=0.5*B+(I-1)*B+XE
      DO 3 N=1,NN,3
      DO 3 J=1,K,1
      LAUC(N,J)=2*J*A-YC
      LAUE(N,J)=2*J*A-YE
      LADC(N,J)=2*(J-1)*A+YC
    3 LADE(N,J)=2*(J-1)*A+YE
      DO 4 N=2,NN,3
      DO 4 J=1,K,1
      LAUC(N,J)=J*A-YC
```

```
      LAUE(N,J)=J*A-YE
      LADC(N,J)=(J-1)*A+YC
    4 LADE(N,J)=(J-1)*A+YE
      DO 5 N=3,NN,3
      DO 5 J=1,K,1
      LAUC(N,J)=(2*J-1)*A-YC
      LAUE(N,J)=(2*J-1)*A-YE
      LADC(N,J)=(2*J-1)*A+YC
    5 LADE(N,J)=(2*J-1)*A+YE
      DO 6 N=1,NN,1
      DO 6 I=1,M,1
      LBR2C(N,I)=LBRC(N,I)**2
      LBR2E(N,I)=LBRE(N,I)**2
      LBL2C(N,I)=LBLC(N,I)**2
    6 LBL2E(N,I)=LBLE(N,I)**2
      DO 7 N=1,NN,1
      DO 7 J=1,K,1
      LAU2C(N,J)=LAUC(N,J)**2
      LAU2E(N,J)=LAUE(N,J)**2
      LAD2C(N,J)=LADC(N,J)**2
    7 LAD2E(N,J)=LADE(N,J)**2
   25 Z=Z+0.10
      DO 8 N=1,NN,1
      F2(N)=(Z+(N-1)*D)**2
      F2C(N)=F2(N)
    8 F2E(N)=F2(N)
      DO 9 N=1,NN,1
      DO 9 I=1,M,1
      DO 9 J=1,K,1
      RUR2C(N,I,J)=F2(N)+LAU2C(N,J)+LBR2C(N,I)
      RUR2E(N,I,J)=F2(N)+LAU2E(N,J)+LBR2E(N,I)
      RUL2C(N,I,J)=F2(N)+LAU2C(N,J)+LBL2C(N,I)
      RUL2E(N,I,J)=F2(N)+LAU2E(N,J)+LBL2E(N,I)
      RDR2C(N,I,J)=F2(N)+LAD2C(N,J)+LBR2C(N,I)
      RDR2E(N,I,J)=F2(N)+LAD2E(N,J)+LBR2E(N,I)
      RDL2C(N,I,J)=F2(N)+LAD2C(N,J)+LBL2C(N,I)
      RDL2E(N,I,J)=F2(N)+LAD2E(N,J)+LBL2E(N,I)
      RE1C(N,I,J)=F/(RUR2C(N,I,J)**6)+F/(RUL2C(N,I,J)**6)+F/(RDR2
     1C(N,I,J)**6)+F/(RDL2C(N,I,J)**6)
      RE1E(N,I,J)=F/(RUR2E(N,I,J)**6)+F/(RUL2E(N,I,J)**6)+F/(RDR2
     1E(N,I,J)**6)+F/(RDL2E(N,I,J)**6)
      EURC(N,I,J)=(1/(RUR2C(N,I,J))**3)*(((9.0*LBR2C(N,I))/(RUR2C(N,I,
     1J))**2)*(LAU2C(N,J)+U*(F2C(N)+LBR2C(N,I)))+(3.0/RUR2C(N,I,J))*(F
     22C(N)-2*U*LBR2C(N,I))+1.0+U)
      EURE(N,I,J)=(1/(RUR2E(N,I,J))**3)*(((9.0*LBR2E(N,I))/(RUR2E(N,I,
     1J))**2)*(LAU2E(N,J)+U*(F2E(N)+LBR2E(N,I)))+(3.0/RUR2E(N,I,J))*(F
     22E(N)-2*U*LBR2E(N,I))+1.0+U)
      EULC(N,I,J)=(1/(RUL2C(N,I,J))**3)*(((9.0*LBL2C(N,I))/(RUL2C(N,I,
     1J))**2)*(LAU2C(N,J)+U*(F2C(N)+LBL2C(N,I)))+(3.0/RUL2C(N,I,J))*(F
     22C(N)-2*U*LBL2C(N,I))+1.0+U)
      EULE(N,I,J)=(1/(RUL2E(N,I,J))**3)*(((9.0*LBL2E(N,I))/(RUL2E(N,I,
     1J))**2)*(LAU2E(N,J)+U*(F2E(N)+LBL2E(N,I)))+(3.0/RUL2E(N,I,J))*(F
     22E(N)-2*U*LBL2E(N,I))+1.0+U)
      EDRC(N,I,J)=(1/(RDR2C(N,I,J))**3)*(((9.0*LBR2C(N,I))/(RDR2C(N,I,
     1J))**2)*(LAD2C(N,J)+U*(F2C(N)+LBR2C(N,I)))+(3.0/RDR2C(N,I,J))*(F
     22C(N)-2*U*LBR2C(N,I))+1.0+U)
```

```
      EDRE(N,I,J)=(1/(RDR2E(N,I,J))**3)*(((9.0*LBR2E(N,I))/(RDR2E(N,I,
     1J))**2)*(LAD2E(N,J)+U*(F2E(N)+LBR2E(N,I)))+(3.0/RDR2E(N,I,J))*(F
     22E(N)-2*U*LBR2E(N,I))+1.0+U)
      EDLC(N,I,J)=(1/(RDL2C(N,I,J))**3)*(((9.0*LBL2C(N,I))/(RDL2C(N,I,
     1J))**2)*(LAD2C(N,J)+U*(F2C(N)+LBL2C(N,I)))+(3.0/RDL2C(N,I,J))*(F
     22C(N)-2*U*LBL2C(N,I))+1.0+U)
    9 EDLE(N,I,J)=(1/(RDL2E(N,I,J))**3)*(((9.0*LBL2E(N,I))/(RDL2E(N,I,
     1J))**2)*(LAD2E(N,J)+U*(F2E(N)+LBL2E(N,I)))+(3.0/RDL2E(N,I,J))*(F
     22E(N)-2*U*LBL2E(N,I))+1.0+U)
      ETOT=0.0
      RETOT=0.0
      ETOTE=0.0
      RETOTE=0.0
      ETOTC=0.0
      RETOTC=0.0
      DO 11 N=1,NN,1
      E(N)=0.0
      RE(N)=0.0
      EC(N)=0.0
      EE(N)=0.0
      REC(N)=0.0
      REE(N)=0.0
      DO 10 I=1,M,1
      DO 10 J=1,K,1
      EC(N)=EC(N)+EURC(N,I,J)+EULC(N,I,J)+EDRC(N,I,J)+EDLC(N,I,J)
      EE(N)=EE(N)+EURE(N,I,J)+EULE(N,I,J)+EDRE(N,I,J)+EDLE(N,I,J)
      REC(N)=REC(N)+REIC(N,I,J)
   10 REE(N)=REE(N)+REIE(N,I,J)
      ETOTC=ETOTC+EC(N)
      ETOTE=ETOTE+EE(N)
      RETOTC=RETOTC+REC(N)
   11 RETOTE=RETOTE+REE(N)
      EFIN=0.0
      ETOT=ETOTC+2.0*ETOTE
      RETOT=RETOTC+2.0*RETOTE
      EFIN=EFIN+RETOT-ETOT
      PRINT 102, ETOT,RETOT,Z,EFIN
      PRINT 103,
      DO 12 N=1,12,1
      ED(N)=REC(N)-EC(N)+2.0*(REE(N)-EE(N))
   12 PRINT 104, N,ED(N)
      IF(Z-Q)25,13,13
   13 END
```

PROGRAM 7

```
      PROGRAM GRAPHITE
C     LINEAR ADATOM ON GRAPHITE, PARALLEL TO EDGE PLANE, PERPENDICULAR
C      TO BASAL PLANES - CC2 IN GAP
  102 FORMAT(//15H  ATTRACTION = E13.5//
     115H  REPULSION  = E13.5//
     228H  TOTAL INTERACTION FOR Z = F6.3/
     39H        = E13.5//)
  103 FORMAT(//34H ENERGY AS FN(DEPTH), N      ENERGY/)
  104 FORMAT(21X,I2,E13.5)
  105 FORMAT(54H N I J     RUR2C          RUL2C          RDR2C          RDL2C)
  106 FORMAT(3I2,4E13.5)
  107 FORMAT(54H N I J      EURC           EULC           EDRC           EDLC)
  108 FORMAT(15H N I J      REIC)
  109 FORMAT(3I2,1E13.5)
      COMMON/A/ LBR(30,9),LBL(30,9),LAUC(30,7),LAUE(30,7),LADC(30,7),
     1LADE(30,7),LBR2(30,9),LBL2(30,9),LAU2C(30,7),LAU2E(30,7),
     2LAD2C(30,7),LAD2E(30,7),F2(30),RUR2C(30,9,7),RUR2E(30,9,7)
      COMMON/B/      RUL2E(30,9,7),RDR2C(30,9,7),RDR2E(30,9,7),
     4RDL2C(30,9,7),RDL2E(30,9,7),REIC(30,9,7),REIE(30,9,7),
     5EUR C(30,9,7),EUR E(30,9,7),EUL C(30,9,7),EUL E(30,9,7),
     6EDR C(30,9,7),EDR E(30,9,7),EDL C(30,9,7),EDL E(30,9,7),
     7EC(30),EE(30),REC(30),REE(30),ED(30),RUL2C(30,9,7)
      TYPE REAL LBR,LBL,LAUC,LAUE,LADC,LADE,LBR2,LBL2,LAU2C,LAU2E,
     1LAD2C,LAD2E
      BANK,(0),/A/
      T=2.79E+5
      F =1.56E+9
      X=0
      YC=3.35
      YE=2.19
      Z=2.3
      D=0.71
      B=2.459
      A=3.35
      NN=30
      K=7
      Q=2.5
      M=9
      U=2.08
      DO 1 N=1,NN,2
      DO 1 I=1,M,1
      LBR(N,I)=I*B-X
    1 LBL(N,I)=(I-1)*B+X
      DO 2 N=2,NN,2
      DO 2 I=1,M,1
      LBR(N,I)=0.5*B+(I-1)*B-X
    2 LBL(N,I)=0.5*B+(I-1)*B+X
      DO 3 N=1,NN,3
      DO 3 J=1,K,1
      LAUC(N,J)=2*J*A-YC
      LAUE(N,J)=2*J*A-YE
      LADC(N,J)=2*(J-1)*A+YC
    3 LADE(N,J)=2*(J-1)*A+YE
      DO 4 N=2,NN,3
      DO 4 J=1,K,1
      LAUC(N,J)=J*A-YC
```

```
      LAUE(N,J)=J*A-YE
      LADC(N,J)=(J-1)*A+YC
    4 LADE(N,J)=(J-1)*A+YE
      DO 5 N=3,NN,3
      DO 5 J=1,K,1
      LAUC(N,J)=(2*J-1)*A-YC
      LAUE(N,J)=(2*J-1)*A-YE
      LADC(N,J)=(2*J-1)*A+YC
    5 LADE(N,J)=(2*J-1)*A+YE
      DO 6 N=1,NN,1
      DO 6 I=1,M,1
      LBR2(N,I)=LBR(N,I)**2
    6 LBL2(N,I)=LBL(N,I)**2
      DO 7 N=1,NN,1
      DO 7 J=1,K,1
      LAU2C(N,J)=LAUC(N,J)**2
      LAU2E(N,J)=LAUE(N,J)**2
      LAD2C(N,J)=LADC(N,J)**2
    7 LAD2E(N,J)=LADE(N,J)**2
   25 Z=Z+0.10
      DO 8 N=1,NN,1
    8 F2(N)=(Z+(N-1)*D)**2
      DO 9 N=1,NN,1
      DO 9 I=1,M,1
      DO 9 J=1,K,1
      RUR2C(N,I,J)=LAU2C(N,J)+LBR2(N,I)+F2(N)
      RUR2E(N,I,J)=LAU2E(N,J)+LBR2(N,I)+F2(N)
      RUL2C(N,I,J)=LAU2C(N,J)+LBL2(N,I)+F2(N)
      RUL2E(N,I,J)=LAU2E(N,J)+LBL2(N,I)+F2(N)
      RDR2C(N,I,J)=LAD2C(N,J)+LBR2(N,I)+F2(N)
      RDR2E(N,I,J)=LAD2E(N,J)+LBR2(N,I)+F2(N)
      RDL2C(N,I,J)=LAD2C(N,J)+LBL2(N,I)+F2(N)
      RDL2E(N,I,J)=LAD2E(N,J)+LBL2(N,I)+F2(N)
      REIC(N,I,J)=F/(RUR2C(N,I,J)**6)+F/(RUL2C(N,I,J)**6)+F/(RDR2C(N,I
     1,J)**6)+F/(RDL2C(N,I,J)**6)
      REIE(N,I,J)=F/(RUR2E(N,I,J)**6)+F/(RUL2E(N,I,J)**6)+F/(RDR2E(N,I
     1,J)**6)+F/(RDL2E(N,I,J)**6)
      EUR C(N,I,J)=(T/(RUR2C(N,I,J))**3)*(2.0-(6.0*(F2(N)+LBR2(N,I)))/
     1RUR2C(N,I,J)+(9.0*(F2(N)+LBR2(N,I))*(F2(N)+LBR2(N,I)+U*LAU2C(N,J
     2)))/(RUR2C(N,I,J)**2))
      EUR E(N,I,J)=(T/(RUR2E(N,I,J))**3)*(2.0-(6.0*(F2(N)+LBR2(N,I)))/
     1RUR2E(N,I,J)+(9.0*(F2(N)+LBR2(N,I))*(F2(N)+LBR2(N,I)+U*LAU2E(N,J
     2)))/(RUR2E(N,I,J)**2))
      EUL C(N,I,J)=(T/(RUL2C(N,I,J))**3)*(2.0-(6.0*(F2(N)+LBL2(N,I)))/
     1RUL2C(N,I,J)+(9.0*(F2(N)+LBL2(N,I))*(F2(N)+LBL2(N,I)+U*LAU2C(N,J
     2)))/(RUL2C(N,I,J)**2))
      EUL E(N,I,J)=(T/(RUL2E(N,I,J))**3)*(2.0-(6.0*(F2(N)+LBL2(N,I)))/
     1RUL2E(N,I,J)+(9.0*(F2(N)+LBL2(N,I))*(F2(N)+LBL2(N,I)+U*LAU2E(N,J
     2)))/(RUL2E(N,I,J)**2))
      EDR C(N,I,J)=(T/(RDR2C(N,I,J))**3)*(2.0-(6.0*(F2(N)+LBR2(N,I)))/
     1RDR2C(N,I,J)+(9.0*(F2(N)+LBR2(N,I))*(F2(N)+LBR2(N,I)+U*LAD2C(N,J
     2)))/(RDR2C(N,I,J)**2))
      EDR E(N,I,J)=(T/(RDR2E(N,I,J))**3)*(2.0-(6.0*(F2(N)+LBR2(N,I)))/
     1RDR2E(N,I,J)+(9.0*(F2(N)+LBR2(N,I))*(F2(N)+LBR2(N,I)+U*LAD2E(N,J
     2)))/(RDR2E(N,I,J)**2))
      EDL C(N,I,J)=(T/(RDL2C(N,I,J))**3)*(2.0-(6.0*(F2(N)+LBL2(N,I)))/
```

```
  1RDL2C(N,I,J)+(9.0*(F2(N)+LBL2(N,I))*(F2(N)+LBL2(N,I)+U*LAD2C(N,J
  2)))/(RDL2C(N,I,J)**2))
 9 EDL E(N,I,J)=(T/(RDL2E(N,I,J))**3)*(2.0-(6.0*(F2(N)+LBL2(N,I)))/
  1RDL2E(N,I,J)+(9.0*(F2(N)+LBL2(N,I))*(F2(N)+LBL2(N,I)+U*LAD2E(N,J
  2)))/(RDL2E(N,I,J)**2))
   ETOTC=0.0
   ETOTE=0.0
   ETOT=0.0
   RETOTC=0.0
   RETOTE=0.0
   RETOT=0.0
   DO 11 N=1,NN,1
   EC(N)=0.0
   EE(N)=0.0
   REC(N)=0.0
   REE(N)=0.0
   DO 10 I=1,M,1
   DO 10 J=1,K,1
   EC(N)=EC(N)+EURC(N,I,J)+EULC(N,I,J)+EDRC(N,I,J)+EDLC(N,I,J)
   EE(N)=EE(N)+EURE(N,I,J)+EULE(N,I,J)+EDRE(N,I,J)+EDLE(N,I,J)
   REC(N)=REC(N)+REIC(N,I,J)
10 REE(N)=REE(N)+REIE(N,I,J)
   ETOTC=ETOTC+EC(N)
   ETOTE=ETOTE+EE(N)
   RETOTC=RETOTC+REC(N)
11 RETOTE=RETOTE+REE(N)
   EFINC=0.0
   EFINE=0.0
   EFIN=0.0
   EFINC=EFINC+RETOTC-ETOTC
   EFINE=EFINE+2.0*RETOTE-2.0*ETOTE
   ETOT=ETOTC+2.0*ETOTE
   RETOT=RETOTC+2.0*RETOTE
   EFIN=EFINC+EFINE
   PRINT 102, ETOT,RETOT,Z,EFIN
   PRINT 103,
   DO 12 N=1,10,1
   ED(N)=REC(N)+2.0*REE(N)-EC(N)-2.0*EE(N)
12 PRINT 104, N,ED(N)
   PRINT 105,
   DO 14 N=1,3,1
   DO 14 I=1,2,1
   DO 14 J=1,2,1
14 PRINT 106, N,I,J,RUR2C(N,I,J),RUL2C(N,I,J),RDR2C(N,I,J),
  1RDL2C(N,I,J)
   PRINT 107,
   DO 15 N=1,3,1
   DO 15 I=1,2,1
   DO 15 J=1,2,1
15 PRINT 106, N,I,J,EURC(N,I,J),EULC(N,I,J),EDRC(N,I,J),EDLC(N,I,J)
   PRINT 108,
   DO 16 N=1,3,1
   DO 16 I=1,2,1
   DO 16 J=1,2,1
16 PRINT 109, N,I,J,REIC(N,I,J)
   IF(Z-Q)25,13,13
13 END
```

PROGRAM 8

```
      PROGRAM GRAPHITE
C     LINEAR ADATOM PERPENDICULAR ON EDGE PLANE - CO2 ON GRAPHITE
  102 FORMAT(//15H  ATTRACTION = E13.5//
     115H  REPULSION  = E13.5//
     236H  TOTAL INTERACTION FOR Z(CENTER) = F6.3/
     39H        = E13.5//)
  103 FORMAT(//34H ENERGY AS FN(DEPTH), N      ENERGY/)
  104 FORMAT(21X,I2,E13.5)
  105 FORMAT(54H N I J     RUR2C          RUL2C          RDR2C          RDL2C)
  106 FORMAT(3I2,4E13.5)
  107 FORMAT(14H N I J      REI)
  108 FORMAT(3I2,1E13.5)
  109 FORMAT(53H N I J      EUR            EUL            EDR            EDL)
      COMMON/A/ LBR(30,9),LBL(30,9),LAU(30,7),LAD(30,7),F2C(30),
     1LAU2(30,7),LAD2(30,7),LBR2(30,9),LBL2(30,9),RUR2C(30,9,7),F2N(30),
     2RUL2C(30,9,7),RDR2C(30,9,7),RDL2C(30,9,7),REI(30,9,7),F2F(30),
     3EUR(30,9,7),EUL(30,9,7),EDR(30,9,7),EDL(30,9,7),E(30)
      COMMON/B/      RUR2N(30,9,7),RUR2F(30,9,7),RUL2N(30,9,7),
     5RUL2F(30,9,7),RDR2N(30,9,7),RDR2F(30,9,7),RDL2N(30,9,7),RDL2F(
     630,9,7),RE(30),ED(30)
      TYPE REAL LBR,LBL,LAU,LAD,LAU2,LAD2,LBR2,LBL2
      BANK,(0),/A/
      T=2,79E+5
      F=1,56E+9
      X=0
      Y=2,472
      ZC=2.7
      ZN=1.54
      ZF=3.86
      D=0,71
      B=2,459
      A=3,35
      NN=30
      K=7
      Q=3,0
      M=9
      U=2,08
      DO 1 N=1,NN,2
      DO 1 I=1,M,1
      LBR(N,I)=I*B-X
    1 LBL(N,I)=(I-1)*B+X
      DO 2 N=2,NN,2
      DO 2 I=1,M,1
      LBR(N,I)=0.5*B+(I-1)*B-X
    2 LBL(N,I)=0.5*B+(I-1)*B+X
      DO 3 N=1,NN,3
      DO 3 J=1,K,1
      LAU(N,J)=2*J*A-Y
    3 LAD(N,J)=2*(J-1)*A+Y
      DO 4 N=2,NN,3
      DO 4 J=1,K,1
      LAU(N,J)=J*A-Y
    4 LAD(N,J)=(J-1)*A+Y
      DO 5 N=3,NN,3
      DO 5 J=1,K,1
      LAU(N,J)=(2*J-1)*A-Y
```

```
 5 LAD(N,J)=(2*J-1)*A+Y
25 ZC=ZC+0.10
   ZN=ZN+0.10
   ZF=ZF+0.10
   DO 6 N=1,NN,1
   F2C(N)=(ZC+(N-1)*D)**2
   F2N(N)=(ZN+(N-1)*D)**2
 6 F2F(N)=(ZF+(N-1)*D)**2
   DO 7 N=1,NN,1
   DO 7 J=1,K,1
   LAU2(N,J)=LAU(N,J)**2
 7 LAD2(N,J)=LAD(N,J)**2
   DO 8 N=1,NN,1
   DO 8 I=1,M,1
   LBR2(N,I)=LBR(N,I)**2
 8 LBL2(N,I)=LBL(N,I)**2
   DO 9 N=1,NN,1
   DO 9 I=1,M,1
   DO 9 J=1,K,1
   RUR2C(N,I,J)=F2C(N)+LAU2(N,J)+LBR2(N,I)
   RUR2N(N,I,J)=F2N(N)+LAU2(N,J)+LBR2(N,I)
   RUR2F(N,I,J)=F2F(N)+LAU2(N,J)+LBR2(N,I)
   RUL2C(N,I,J)=F2C(N)+LAU2(N,J)+LBL2(N,I)
   RUL2N(N,I,J)=F2N(N)+LAU2(N,J)+LBL2(N,I)
   RUL2F(N,I,J)=F2F(N)+LAU2(N,J)+LBL2(N,I)
   RDR2C(N,I,J)=F2C(N)+LAD2(N,J)+LBR2(N,I)
   RDR2N(N,I,J)=F2N(N)+LAD2(N,J)+LBR2(N,I)
   RDR2F(N,I,J)=F2F(N)+LAD2(N,J)+LBR2(N,I)
   RDL2C(N,I,J)=F2C(N)+LAD2(N,J)+LBL2(N,I)
   RDL2N(N,I,J)=F2N(N)+LAD2(N,J)+LBL2(N,I)
   RDL2F(N,I,J)=F2F(N)+LAD2(N,J)+LBL2(N,I)
   REI(N,I,J)=F/(RUR2C(N,I,J)**6)+F/(RUR2N(N,I,J)**6)+F/(RUR2F(N,I,
  1J)**6)+F/(RUL2C(N,I,J)**6)+F/(RUL2N(N,I,J)**6)+F/(RUL2F(N,I,J)**
  26)+F/(RDR2C(N,I,J)**6)+F/(RDR2N(N,I,J)**6)+F/(RDR2F(N,I,J)**6)+F
  3/(RDL2C(N,I,J)**6)+F/(RDL2N(N,I,J)**6)+F/(RDL2F(N,I,J)**6)
   EUR(N,I,J)=(T/(RUR2C(N,I,J))**3)*((9.0/(RUR2C(N,I,J))**2)*(F2C(N)
  1+LBR2(N,I))*(LAU2(N,J)+LBR2(N,I)+U*F2C(N))-(6.0/RUR2C(N,I,J))*
  2(LBR2(N,I)+U*F2C(N))+1.0+U)+(T/(RUR2N(N,I,J))**3)*((9.0/(RUR2N(N
  3,I,J))**2)*(F2N(N)+LBR2(N,I))*(LAU2(N,J)+LBR2(N,I)+U*F2N(N))-(
  46.0/RUR2N(N,I,J))*(LBR2(N,I)+U*F2N(N))+1.0+U)+(T/(RUR2F(N,I,J))*
  5*3)*((9.0/(RUR2F(N,I,J))**2)*(F2F(N)+LBR2(N,I))*(LAU2(N,J)+LBR2
  6(N,I)+U*F2F(N))-(6.0/RUR2F(N,I,J))*(LBR2(N,I)+U*F2F(N))+1.0+U)
   EUL(N,I,J)=(T/(RUL2C(N,I,J))**3)*((9.0/(RUL2C(N,I,J))**2)*(F2C(N)
  1+LBL2(N,I))*(LAU2(N,J)+LBL2(N,I)+U*F2C(N))-(6.0/RUL2C(N,I,J))*
  2(LBL2(N,I)+U*F2C(N))+1.0+U)+(T/(RUL2N(N,I,J))**3)*((9.0/(RUL2N(N
  3,I,J))**2)*(F2N(N)+LBL2(N,I))*(LAU2(N,J)+LBL2(N,I)+U*F2N(N))-(
  46.0/RUL2N(N,I,J))*(LBL2(N,I)+U*F2N(N))+1.0+U)+(T/(RUL2F(N,I,J))*
  5*3)*((9.0/(RUL2F(N,I,J))**2)*(F2F(N)+LBL2(N,I))*(LAU2(N,J)+LBL2
  6(N,I)+U*F2F(N))-(6.0/RUL2F(N,I,J))*(LBL2(N,I)+U*F2F(N))+1.0+U)
   EDR(N,I,J)=(T/(RDR2C(N,I,J))**3)*((9.0/(RDR2C(N,I,J))**2)*(F2C(N)
  1+LBR2(N,I))*(LAD2(N,J)+LBR2(N,I)+U*F2C(N))-(6.0/RDR2C(N,I,J))*
  2(LBR2(N,I)+U*F2C(N))+1.0+U)+(T/(RDR2N(N,I,J))**3)*((9.0/(RDR2N(N
  3,I,J))**2)*(F2N(N)+LBR2(N,I))*(LAD2(N,J)+LBR2(N,I)+U*F2N(N))-(
  46.0/RDR2N(N,I,J))*(LBR2(N,I)+U*F2N(N))+1.0+U)+(T/(RDR2F(N,I,J))*
  5*3)*((9.0/(RDR2F(N,I,J))**2)*(F2F(N)+LBR2(N,I))*(LAD2(N,J)+LBR2
  6(N,I)+U*F2F(N))-(6.0/RDR2F(N,I,J))*(LBR2(N,I)+U*F2F(N))+1.0+U)
```

```
 9 EDL(N,I,J)=(T/(RDL2C(N,I,J))**3)*((9.0/(RDL2C(N,I,J))**2)*(F2C(N)
  1+LBL2(N,I))*(LAD2(N,J)+LBL2(N,I)+U*F2C(N))-(6.0/RDL2C(N,I,J))*
  2(LBL2(N,I)+U*F2C(N))+1.0+U)+(T/(RDL2N(N,I,J))**3)*((9.0/(RDL2N(N
  3,I,J))**2)*(F2N(N)+LBL2(N,I))*(LAD2(N,J)+LBL2(N,I)+U*F2N(N))-(
  46.0/RDL2N(N,I,J))*(LBL2(N,I)+U*F2N(N))+1.0+U)+(T/(RDL2F(N,I,J))*
  5*3)*((9.0/(RDL2F(N,I,J))**2)*(F2F(N)+LBL2(N,I))*(LAD2(N,J)*LBL2
  6(N,I)+U*F2F(N))-(6.0/RDL2F(N,I,J))*(LBL2(N,I)+U*F2F(N))+1.0+U)
   ETOT=0.0
   RETOT=0.0
   DO 11 N=1,NN,1
   E(N)=0.0
   RE(N)=0.0
   DO 10 I=1,M,1
   DO 10 J=1,K,1
   E(N)=E(N)+EUR(N,I,J)+EUL(N,I,J)+EDR(N,I,J)+EDL(N,I,J)
10 RE(N)=RE(N)+REI(N,I,J)
   ETOT=ETOT+E(N)
11 RETOT=RETOT+RE(N)
   EFIN=0.0
   EFIN=EFIN+RETOT-ETOT
   PRINT 102, ETOT,RETOT,ZC,EFIN
   PRINT 103,
   DO 12 N=1,10,1
   ED(N)=RE(N)-E(N)
12 PRINT 104, N, ED(N)
   DO 14 N=1,3,1
   DO 14 I=1,3,1
   DO 14 J=1,3,1
   PRINT 105,
   PRINT 106, N,I,J,RUR2C(N,I,J),RUL2C(N,I,J),RDR2C(N,I,J),
  1RDL2C(N,I,J)
   PRINT 107,
   PRINT 108, N,I,J,REI(N,I,J)
   PRINT 109,
14 PRINT 106, N,I,J,EUR(N,I,J),EUL(N,I,J),EDR(N,I,J),EDL(N,I,J)
   IF(ZC-Q)25,13,13
13 END
```

PROGRAM 9

```
      PROGRAM GRAPHITE
C     LINEAR ADATOM PARALLEL TO BASAL PLANE - ANISOTROPIC CO2 ON
C     ISOTROPIC GRAPHITE
  102 FORMAT(//15H  ATTRACTION = E13.5//
     115H  REPULSION  = E13.5/
     228H  TOTAL INTERACTICN FOR Z = F6.3/
     39H        = E13.5//)
  103 FORMAT(//34H ENERGY AS FN(DEPTH), N     ENERGY/)
  104 FORMAT(21X,I2,E13.5)
      COMMON/B/ LBG2C(10),LBG2E(10),LBP2C(10),LBP2E(10),LBR2C(10),LBR2
     1E(10),LBB2C(10),LBB2E(10),LAG2C(10),LAG2E(10),LAP2C(10),LAP2E(10
     2),LAR2C(10),LAR2E(10),LAB2C(10),LAB2E(10),F2(10),RGC2(10,10,10),
     3RGE2(10,10,10),RPC2(10,10,10),RPE2(10,10,10),RRC2(10,10,10),
     4RRE2(10,10,10),RBC2(10,10,10),RBE2(10,10,10),REIC(10,10,10),
     5REIE(10,10,10),EGC(10,10,10),EGE(10,10,10),EPC(10,10,10),
     6EPE(10,10,10),ERC(10,10,10),ERE(10,10,10),EBC(10,10,10)
      COMMON/A/ EBE(10,10,10),LAVPC2(10),LAVRC2(10),RVPC2(10,10),
     1RVPE2(10,10),RVRC2(10,10),RVRE2(10,10),EVPC(10,10),
     2EVRC(10,10),EVPE(10,10),EVRE(10,10),EC(10),EE(10),E(10),
     3REC(10),REE(10),RE(10),EVC(10),EVE(10),REVC(10),REVE(10),
     4REIVC(10,10),REIVE(10,10),ED(10),LBG2EP(10),LBP2EP(10),LBR2EP(10),
     5LBB2EP(10),RGE2P(10,10,10),RPE2P(10,10,10),RRE2P(10,10,10),RBE2P(1
     60,10,10)
      TYPE REAL LBG2C,LBG2E,LBP2C,LPB2E,LBR2C,LBR2E,LBB2C,LBB2E,
     1LAG2C,LAG2E,LAP2C,LAP2E,LAR2C,LAR2E,LAB2C,LAB2E,LAVPC2,
     2LAVRC2,LBG2EP,LBP2EP,LBB2EP
      BANK,(0),/A/
      T=1.86E+5
      F=2.08E+9
      XC=0
      YC=0
      XE=1.16
      XEP=-1.16
      YE=0
      Z=3.2
      D=3.35
      A=4.26
      B=2.459
      NN=10
      K=10
      M=10
      Q=3.6
      J=2.08
      C=0.71
      DO 1 I=1,M,1
      LBG2C(I)=(0.5*B-XC+(I-1)*B)**2
      LBG2E(I)=(0.5*B-XE+(I-1)*B)**2
      LBG2EP(I)=(0.5*B-XEP+(I-1)*B)**2
      LBP2C(I)=(B-XC+(I-1)*B)**2
      LBP2E(I)=(B-XE+(I-1)*B)**2
      LBP2EP(I)=(B-XEP+(I-1)*B)**2
      LBR2C(I)=LBP2C(I)
      LBR2E(I)=LBP2E(I)
      LBR2EP(I)=LBP2EP(I)
      LBB2C(I)=LBG2C(I)
      LBB2E(I)=LBG2E(I)
```

```
 1 LBB2EP(I)=LBG2EP(I)
   DO 2 J=1,K,1
   LAG2C(J)=(C-YC+(J-1)*A)**2
   LAG2E(J)=(C-YE+(J-1)*A)**2
   LAP2C(J)=(2.0*C-YC+(J-1)*A)**2
   LAP2E(J)=(2.0*C-YE+(J-1)*A)**2
   LAR2C(J)=(4.0*C-YC+(J-1)*A)**2
   LAR2E(J)=(4.0*C-YE+(J-1)*A)**2
   LAB2C(J)=(5.0*C-YC+(J-1)*A)**2
   LAB2E(J)=(5.0*C-YE+(J-1)*A)**2
   LAVPC2(J)=(1.42+(J-1)*A)**2
 2 LAVRC2(J)=(2.84+(J-1)*A)**2
25 Z=Z+0.10
   DO 3 N=1,NN,1
 3 F2(N)=(Z+(N-1)*D)**2
   DO 4 N=1,NN,1
   DO 4 I=1,M,1
   DO 4 J=1,K,1
   RGC2(N,I,J)=F2(N)+LBG2C(I)+LAG2C(J)
   RGE2(N,I,J)=F2(N)+LBG2E(I)+LAG2E(J)
   RGE2P(N,I,J)=F2(N)+LBG2EP(I)+LAG2E(J)
   RPC2(N,I,J)=F2(N)+LBP2C(I)+LAP2C(J)
   RPE2(N,I,J)=F2(N)+LBP2E(I)+LAP2E(J)
   RPE2P(N,I,J)=F2(N)+LBP2EP(I)+LAP2E(J)
   RRC2(N,I,J)=F2(N)+LBR2C(I)+LAR2C(J)
   RRE2(N,I,J)=F2(N)+LBR2E(I)+LAR2E(J)
   RRE2P(N,I,J)=F2(N)+LBR2EP(I)+LAR2E(J)
   RBC2(N,I,J)=F2(N)+LBB2C(I)+LAB2C(J)
   RBE2(N,I,J)=F2(N)+LBB2E(I)+LAB2E(J)
   RBE2P(N,I,J)=F2(N)+LBB2EP(I)+LAB2E(J)
   RBIC(N,I,J)=F/(RGC2(N,I,J)**6)+F/(RPC2(N,I,J)**6)+F/(RRC2(N,I,J)
  1**6)+F/(RBC2(N,I,J)**6)
   RBIE(N,I,J)=F/(RGE2(N,I,J)**6)+F/(RPE2(N,I,J)**6)+F/(RRE2(N,I,J)
  1**6)+F/(RBE2(N,I,J)**6)+F/RGE2P(N,I,J)**6+F/RPE2P(N,I,J)**6+F/RRE2
  2P(N,I,J)**6+F/RBE2P(N,I,J)**6
   EGC(N,I,J)=(T/RGC2(N,I,J)**3)*(2.0+U-(6.0/RGC2(N,I,J))*(F2(N)+
  1LBG2C(I)+U*LAG2C(J))+(9.0*F2(N)/RGC2(N,I,J)**2)*(LBG2C(I)+U*LA
  2G2C(J))+9.0*F2(N)/RGC2(N,I,J)+(9.0/RGC2(N,I,J)**2)*(LAG2C(J)*L
  3BG2C(I)*(1.0+U)+LBG2C(I)**2+U*LAG2C(J)**2))
   EGE(N,I,J)=(T/RGE2(N,I,J)**3)*(2.0+U-(6.0/RGE2(N,I,J))*(F2(N)+
  1LBG2E(I)+U*LAG2E(J))+(9.0*F2(N)/RGE2(N,I,J)**2)*(LBG2E(I)+U*LA
  2G2E(J))+9.0*F2(N)/RGE2(N,I,J)+(9.0/RGE2(N,I,J)**2)*(LAG2E(J)*L
  3BG2E(I)*(1.0+U)+LBG2E(I)**2+U*LAG2E(J)**2))+(T/RGE2P(N,I,J)**3)*(2
  4.0+U-(6.0/RGE2P(N,I,J))*(F2(N)+LBG2EP(I)+U*LAG2E(J))+(9.0*F2(N)/RG
  5E2P(N,I,J)**2)*(LBG2EP(I)+U*LAG2E(J))+9.0*F2(N)/RGE2P(N,I,J)+(9.0/
  6RGE2P(N,I,J)**2)*(LAG2E(J)*LBG2EP(I)*(1.0+U)+LBG2EP(I)**2+U*LAG2E(
  7J)**2))
   EPC(N,I,J)=(T/RPC2(N,I,J)**3)*(2.0+U-(6.0/RPC2(N,I,J))*(F2(N)+
  1LBP2C(I)+U*LAP2C(J))+(9.0*F2(N)/RPC2(N,I,J)**2)*(LBP2C(I)+U*LA
  2P2C(J))+9.0*F2(N)/RPC2(N,I,J)+(9.0/RPC2(N,I,J)**2)*(LAP2C(J)*L
  3BP2C(I)*(1.0+U)+LBP2C(I)**2+U*LAP2C(J)**2))
   EPE(N,I,J)=(T/RPE2(N,I,J)**3)*(2.0+U-(6.0/RPE2(N,I,J))*(F2(N)+
  1LBP2E(I)+U*LAP2E(J))+(9.0*F2(N)/RPE2(N,I,J)**2)*(LBP2E(I)+U*LA
  2P2E(J))+9.0*F2(N)/RPE2(N,I,J)+(9.0/RPE2(N,I,J)**2)*(LAP2E(J)*L
  3BP2E(I)*(1.0+U)+LBP2E(I)**2+U*LAP2E(J)**2))+(T/RPE2P(N,I,J)**3)*(2
  4.0+U-(6.0/RPE2P(N,I,J))*(F2(N)+LBP2EP(I)+U*LAP2E(J))+(9.0*F2(N)/RP
```

```
 5=2P(N,I,J)**2)*(LBP2EP(I)+U*LAP2E(J))+9.0*F2(N)/RPE2P(N,I,J)+(9.0/
 6RPE2P(N,I,J)**2)*(LAP2E(J)*LBP2EP(I)*(1.0+U)+LBP2EP(I)**2+U*LAP2E(
 7J)**2))
  ERC(N,I,J)=(T/RRC2(N,I,J)**3)*(2.0+U-(6.0/RRC2(N,I,J))*(F2(N)+
 1LBR2C(I)+U*LAR2C(J))+(9.0*F2(N)/RRC2(N,I,J)**2)*(LBR2C(I)+U*LA
 2R2C(J))+9.0*F2(N)/RRC2(N,I,J)+(9.0/RRC2(N,I,J)**2)*(LAR2C(J)*L
 3BR2C(I)*(1.0+U)+LBR2C(I)**2+U*LAR2C(J)**2))
  ERE(N,I,J)=(T/RRE2(N,I,J)**3)*(2.0+U-(6.0/RRE2(N,I,J))*(F2(N)+
 1LBR2E(I)+U*LAR2E(J))+(9.0*F2(N)/RRE2(N,I,J)**2)*(LBR2E(I)+U*LA
 2R2E(J))+9.0*F2(N)/RRE2(N,I,J)+(9.0/RRE2(N,I,J)**2)*(LAR2E(J)*L
 3BR2E(I)*(1.0+U)+LBR2E(I)**2+U*LAR2E(J)**2))+(T/RRE2P(N,I,J)**3)*(2
 4.0+U-(6.0/RRE2P(N,I,J))*(F2(N)+LBR2EP(I)+U*LAR2E(J))+(9.0*F2(N)/RR
 5E2P(N,I,J)**2)*(LBR2EP(I)+U*LAR2E(J))+9.0*F2(N)/RRE2P(N,I,J)+(9.0/
 6RRE2P(N,I,J)**2)*(LAR2E(J)*LBR2EP(I)*(1.0+U)+LBR2EP(I)**2+U*LAR2E(
 7J)**2))
  EBC(N,I,J)=(T/RBC2(N,I,J)**3)*(2.0+U-(6.0/RBC2(N,I,J))*(F2(N)+
 1LBB2C(I)+U*LAB2C(J))+(9.0*F2(N)/RBC2(N,I,J)**2)*(LBB2C(I)+U*LA
 2B2C(J))+9.0*F2(N)/RBC2(N,I,J)+(9.0/RBC2(N,I,J)**2)*(LAB2C(J)*L
 3BB2C(I)*(1.0+U)+LBB2C(I)**2+U*LAB2C(J)**2))
4 EBE(N,I,J)=(T/RBE2(N,I,J)**3)*(2.0+U-(6.0/RBE2(N,I,J))*(F2(N)+
 1LBB2E(I)+U*LAB2E(J))+(9.0*F2(N)/RBE2(N,I,J)**2)*(LBB2E(I)+U*LA
 2B2E(J))+9.0*F2(N)/RBE2(N,I,J)+(9.0/RBE2(N,I,J)**2)*(LAB2E(J)*L
 3BB2E(I)*(1.0+U)+LBB2E(I)**2+U*LAB2E(J)**2))+(T/RBE2P(N,I,J)**3)*(2
 4.0+U-(6.0/RBE2P(N,I,J))*(F2(N)+LBB2EP(I)+U*LAB2E(J))+(9.0*F2(N)/RB
 5E2P(N,I,J)**2)*(LBB2EP(I)+U*LAB2E(J))+9.0*F2(N)/RBE2P(N,I,J)+(9.0/
 6RBE2P(N,I,J)**2)*(LAB2E(J)*LBB2EP(I)*(1.0+U)+LBB2EP(I)**2+U*LAB2E(
 7J)**2))
  LBVE2=XE**2
  DO 6 N=1,NN,1
  DO 6 J=1,K,1
  RVPC2(N,J)=F2(N)+LAVPC2(J)
  RVPE2(N,J)=RVPC2(N,J)+LBVE2
  RVRC2(N,J)=F2(N)+LAVRC2(J)
  RVRE2(N,J)=RVRC2(N,J)+LBVE2
  EVPC(N,J)=(T/RVPC2(N,J)**3)*(2.0+U-(6.0/RVPC2(N,J))*(F2(N)+
 1J*LAVPC2(J))+9.0*F2(N)*U*LAVPC2(N)/RVPC2(N,J)**2+9.0*F2(N)/
 2RVPC2(N,J)+9.0*U*(LAVPC2(J))**2/RVPC2(N,J)**2)
  EVRC(N,J)=(T/RVRC2(N,J)**3)*(2.0+U-(6.0/RVRC2(N,J))*(F2(N)+
 1J*LAVRC2(J))+9.0*F2(N)*U*LAVRC2(J)/RVRC2(N,J)**2+9.0*F2(N)/
 2RVRC2(N,J)+9.0*U*(LAVRC2(J))**2/RVRC2(N,J)**2)
  EVPE(N,J)=(T/RVPE2(N,J)**3)*(2.0+U-(6.0/RVPE2(N,J))*(F2(N)+
 1J*LAVPC2(J))+9.0*F2(N)*U*LAVPC2(J)/RVPE2(N,J)**2+9.0*F2(N)/
 2RVPE2(N,J)+9.0*U*(LAVPC2(J))**2/RVPE2(N,J)**2)
  EVRE(N,J)=(T/RVRE2(N,J)**3)*(2.0+U-(6.0/RVRE2(N,J))*(F2(N)+
 1J*LAVRC2(J))+9.0*F2(N)*U*LAVRC2(J)/RVRE2(N,J)**2+9.0*F2(N)/
 2RVRE2(N,J)+9.0*U*(LAVRC2(J))**2/RVRE2(N,J)**2)
  REIVC(N,J)=F/(RVPC2(N,J)**6)+F/(RVRC2(N,J)**6)
6 REIVE(N,J)=F/(RVPE2(N,J)**6)+F/(RVRE2(N,J)**6)
  ETOTE=0.0
  ETOTC=0.0
  ETOT=0.0
  RETOTE=0.0
  RETOTC=0.0
  RETOT=0.0
  DO 9 N=1,NN,1
  EC(N)=0.0
```

```
      EE(N)=0.0
      E(N)=0.0
      REC(N)=0.0
      REE(N)=0.0
      RE(N)=0.0
      EVC(N)=0.0
      EVE(N)=0.0
      REVC(N)=0.0
      REVE(N)=0.0
      DO 7 I=1,M,1
      DO 7 J=1,K,1
      EC(N)=EC(N)+4.0*(EGC(N,I,J)+EPC(N,I,J)+ERC(N,I,J)+EBC(N,I,J))
      EE(N)=EE(N)+2.0*(EGE(N,I,J)+EPE(N,I,J)+ERE(N,I,J)+EBE(N,I,J))
      REC(N)=REC(N)+4.0*REIC(N,I,J)
    7 REE(N)=REE(N)+2.0*REIE(N,I,J)
      DO 8 J=1,K,1
      EVC(N)=EVC(N)+(EVPC(N,J)+EVRC(N,J))*2.0
      EVE(N)=EVE(N)+(EVPE(N,J)+EVRE(N,J))*2.0
      REVC(N)=REVC(N)+2.0*REIVC(N,J)
    8 REVE(N)=REVE(N)+2.0*REIVE(N,J)
      ETOTC=ETOTC+EC(N)+EVC(N)
      RETOTC=RETOTC+REC(N)+REVC(N)
      ETOTE=ETOTE+EE(N)+EVE(N)
    9 RETOTE=RETOTE+REE(N)+REVE(N)
      EFIN=0.0
      ETOT=ETOT+ETOTC+2.0*ETOTE
      RETOT=RETOT+RETOTC+2.0*RETOTE
      EFIN=EFIN+RETOT-ETOT
      PRINT 102,ETOT,RETOT,Z,EFIN
      PRINT 103,
      DO 10 N=1,10,1
      ED(N)=REC(N)+REVC(N)-EC(N)-EVC(N)+2.0*(REE(N)+REVE(N)-EE(N)-EVE(
     1N))
   10 PRINT 104,N,ED(N)
      IF(Z-Q)25,11,11
   11 END
```

PROGRAM 10

```
      PROGRAM GRAPHITE
C     LINEAR ADATOM PERPENDICULAR TO BASAL PLANE - CO2 ON ISOTROPIC GRA
C     PHITE
  102 FORMAT(//15H  ATTRACTION = E13.5//
     115H  REPULSION  = E13.5//
     236H  TOTAL INTERACTION FOR Z(CENTER) = F6.3/
     39H        = E13.5//)
  103 FORMAT(//34H ENERGY AS FN(DEPTH), J      ENERGY/)
  104 FORMAT(21X,I2,E13.5)
  105 FORMAT(41H N I J        YC              YN              YF)
  106 FORMAT(3I2,3E13.5)
  107 FORMAT(41H N I J        EC              EN              EF)
  108 FORMAT(41H N I J       REC             REN             REF)
      DIMENSION Q(10,10),REP(10,1),  R(10,10),S(10,10),RR(10,10),
     1ZC(10),ZN(10),ZF(10),YC(10,10,10),YN(10,10,10),YF(10,10,10),
     2EC(10,10,10),EN(10,10,10),EF(10,10,10),REF(10,10,10),REN(10,10,
     310),REC(10,10,10),EP(10,1),EP2(10),REP2(10),ED(10)
      G=4.3
      T=1.86E+5
      F=2.08E+9
      U=2.08
      NN=10
      K=10
      M=10
      DO 1 N=1,NN,1
      DO 1 I=1,N,1
    1 Q(N,I)=12
      DO 2 N=1,NN,1
    2 Q(N,1)=6
      DO 3 J=1,K,1
      ZC(J)=3.70+(J-1)*3.35
      ZN(J)=2.54+(J-1)*3.35
    3 ZF(J)=4.86+(J-1)*3.35
      DO 4 N=1,NN,1
    4 S(N,1)=((3.0/2.0)*N-(3.0/4.0)-((-1.0)**N)/4.0)
      DO 5 N=1,NN,1
      DO 5 I=1,N,1
      RR(N,I)=(S(N,1)+((-1)**N+(-1)**(N+I))/4.0)**2+(0.75)*((I-1)**2)
    5 R(N,I)=(SQRTF(RR(N,I)))*1.42
   13 DO 6 N=1,NN,1
      DO 6 I=1,N,1
      DO 6 J=1,K,1
      YC(N,I,J)=SQRTF(ZC(J)**2+(R(N,I))**2)
      YN(N,I,J)=SQRTF(ZN(J)**2+(R(N,I))**2)
      YF(N,I,J)=SQRTF(ZF(J)**2+(R(N,I))**2)
      EC(N,I,J)=Q(N,I)*(T/YC(N,I,J)**6)*(2.0+U-6.0*(R(N,I)**2+U*ZC(J)
     1**2)/YC(N,I,J)**2+9.0*ZC(J)**2*R(N,I)**2*(1.0+U)/YC(N,I,J)**4+9
     2.0*(R(N,I)**4+U*ZC(J)**4)/YC(N,I,J)**4)
      EN(N,I,J)=Q(N,I)*(T/YN(N,I,J)**6)*(2.0+U-6.0*(R(N,I)**2+U*ZN(J)
     1**2)/YN(N,I,J)**2+9.0*ZN(J)**2*R(N,I)**2*(1.0+U)/YN(N,I,J)**4+9
     2.0*(R(N,I)**4+U*ZN(J)**4)/YN(N,I,J)**4)
      EF(N,I,J)=Q(N,I)*(T/YF(N,I,J)**6)*(2.0+U-6.0*(R(N,I)**2+U*ZF(J)
     1**2)/YF(N,I,J)**2+9.0*ZF(J)**2*R(N,I)**2*(1.0+U)/YF(N,I,J)**4+9
     2.0*(R(N,I)**4+U*ZF(J)**4)/YF(N,I,J)**4)
      REC(N,I,J)=(Q(N,I)*F)/(YC(N,I,J)**12)
      REN(N,I,J)=(Q(N,I)*F)/(YN(N,I,J)**12)
```

```
 6 REF(N,I,J)=(Q(N,I)*F)/(YF(N,I,J)**12)
   ETOT=0.0
   RETOT=0.0
   DO 7 N=1,NN,1
   EP(N,1)=0.0
   REP(N,1)=0.0
   DO 7 I=1,N,1
   EP(N,1)=EP(N,1)+EC(N,I,1)+EN(N,I,1)+EF(N,I,1)
 7 REP(N,1)=REP(N,1)+REC(N,I,1)+REN(N,I,1)+REF(N,I,1)
   DO 9 J=1,K,1
   EP2(J)=0.0
   REP2(J)=0.0
   DO 8 N=1,NN,1
   DO 8 I=1,N,1
   EP2(J)=EP2(J)+EC(N,I,J)+EN(N,I,J)+EF(N,I,J)
 8 REP2(J)=REP2(J)+REC(N,I,J)+REN(N,I,J)+REF(N,I,J)
   ETOT=ETOT+EP2(J)
 9 RETOT=RETOT+REP2(J)
   EFIN=RETOT-ETOT
   PRINT 102,ETOT,RETOT,ZC(1),EFIN
   PRINT 103,
   DO 10 J=1,10,1
   ED(J)=REP2(J)-EP2(J)
10 PRINT 104,J,ED(J)
   DO 14 N=1,3,2
   DO 14 I=1,N,1
   DO 14 J=1,2,1
   PRINT 105,
   PRINT 106, N,I,J,YC(N,I,J),YN(N,I,J),YF(N,I,J)
   PRINT 107,
   PRINT 106, N,I,J,EC(N,I,J),EN(N,I,J),EF(N,I,J)
   PRINT 108,
14 PRINT 106, N,I,J,REC(N,I,J),REN(N,I,J),REF(N,I,J)
   DO 11 J=1,K,1
   ZC(J)=ZC(J)+0.10
   ZN(J)=ZN(J)+0.10
11 ZF(J)=ZF(J)+0.10
   IF(ZC(1)-Q)13,12,12
12 END
```

Appendix B

SUMMARY OF ATTRACTIVE AND REPULSIVE CONSTANTS USED

We define the following abbreviations: A = Anisotropic; I = Isotropic; G = Graphite; C = CO_2. The units of the constants are (cal/mole)$\mathring{A}^6$ for attraction, and (cal/mole)$\mathring{A}^{12}$ for repulsion.

System	Attractive Constant $\times 10^{-5}$	Repulsive Constant $\times 10^{-9}$
Ne + AG	0.558	0.150
Ne + IG	2.22	0.200
A + AG	2.33	1.11
A + IG	7.43	1.19
Kr + AG	3.52	2.02
Xe + AG	5.72	4.58
AC + AG	2.79	1.56
IC + AG	3.79	1.67
AC + IG	1.86	2.08
IC + IG	2.53	2.23

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Research Laboratory Washington, D. C. 20390	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

ANISOTROPY IN PHYSICAL ADSORPTION ON GRAPHITE

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

An interim report on a continuing NRL Problem.

5. AUTHOR(S) *(First name, middle initial, last name)*

Edwin F. Meyer

6. REPORT DATE July 31, 1967	7a. TOTAL NO. OF PAGES 60	7b. NO. OF REFS 17

8a. CONTRACT OR GRANT NO. NRL Problem C05-18 b. PROJECT NO. RR 001-01-43-4702 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6547 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research) Washington, D. C. 20360

13. ABSTRACT

Anisotropy of polarizability has been taken into account in calculating the relative strengths of adsorption of Ne, A, Kr, Xe, and CO_2 on several possible sites in the graphite lattice. A 6-12 potential, modified to include an angular dependence arising from anisotropy considerations, was summed over the lattice. As a direct result of the anisotropy, sites on the plane consisting of edges of basal planes exhibit a higher energy of adsorption at 0° K for all the gases considered. Calculations ignoring anisotropy have shown that the nature of the results depends markedly on this characteristic of graphite.

For the inert gases at -196° C, adsorption is still favored on the edge plane unless the adsorption is considered to be immobile. In contrast, for CO_2 at 0° C entropy effect predominates and the basal plane offers the more favorable sites for adsorption. These calculations have ignored any unusual edge effects which may overwhelm the anisotropy effects; in the absence of such effects anisotropy is able to account for the existance of two types of sites on graphite, the relative stability of which depends on temperature.

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S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Anistropic polarizability						
Adsorption						
Isotropic adatom						
Anisotropic admolecule						
Basal plane						
Edge plane						
Carbon						
Graphite						

DD FORM 1 NOV 65 1473 (BACK) (PAGE 2)

GPO 928-645

Security Classification