

Stochastic Search for Isomers on a Quantum Mechanical Surface

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In studying molecules with unusual bonding and structures, it is desirable to be able to find all the isomers that are minima on the energy surface. A stochastic search procedure is described for seeking all the isomers on a surface defined by quantum mechanical calculations involving random kicks followed by optimization. It has been applied to searching for singlet structures for C_6 using the restricted Hartree–Fock/6-311G basis set. In addition to the linear chain and ring previously investigated, 11 additional structures (A–K) were located at this level. These provide a basis for discussing qualitative bonding motifs for this carbon cluster. The application of a similar idea to searching for transition states is discussed.

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Introduction

Many methods of searching for conformers (minimum energy points) on a molecular mechanics energy surface have been described. Most currently used procedures for searching for conformers are based on the use of random numbers. One procedure called the stochastic search method^{1a–e} is general, simple to implement, and fast. It involves repeatedly moving all the atoms of a structure randomly followed by refinement with an optimizer. Although it efficiently finds conformers, it gives no information about any structures that are isomers of the input structure.

There are many cases where it is desirable to locate all the isomers of a particular composition. When molecules have well-defined single, double, and triple bonds between atoms, it is easy to write down all of the isomers. However, there are many important cases, including carbocations, where there are partial bonds or bonds of nonintegral order and unusual geometries. Molecular mechanics cannot be applied in these cases and it is necessary to use quantum mechanics to treat them theoretically. *Ab initio* quantum mechanical programs such as GAUSSIAN do not need to be told about the kinds of bonds between atoms. If the positions of all the atoms are input, a calculation can be done to yield the energy and other properties. Optimization can be requested to seek a minimum energy structure. Vibration frequency calculations can be done to determine whether a stationary point obtained is a minimum or a transition state.

Method

How can one find all the isomers (minima) on the energy surface for molecules? This article reports a random search procedure for

seeking all the minima on a quantum mechanical energy surface. The method is analogous to the stochastic search procedure previously developed for molecular mechanics surfaces. The procedure can begin with any structure for the molecule. It is submitted to GAUSSIAN optimization. The minimum energy structure obtained is then subject to an operation called a kick. Each atom is moved a random distance in a random direction. The only limitation is the maximum distance the atoms are to be moved. Each atom is kicked to a position within a sphere of radius R around its initial position, where R is the maximum kick distance. Calculating such randomly moved positions is extremely simple. One generates random values between $-R$ and $+R$ for the displacements along the x , y , and z axes. An atom kicked in such a way will, in fact, wind up within a cube $2R$ on a side instead of a sphere of radius R . The orientation of this cube would be changed by rotating the molecule in Cartesian space. To have kicked positions fall within a sphere instead of a cube, one need only calculate the distance moved [$\sqrt{x^2 + y^2 + z^2}$]. If it is greater than R , this kick is rejected and a new set of three random displacements is chosen. Effectively, we are cutting off the corners of the cube and making it into a sphere. After all the atoms are randomly moved in this way, quantum mechanical optimization is carried out again. There are two possible results: The structure can go back to its previous state or it can go to a different structure. The new structure may differ from the initial structure only in a permutation of atoms so that it is the same isomer. However, bonds can be made or broken or both, leading to a different isomer. If a different structure is formed, it is compared with those in a library of isomers. If it is not there, it is added. Any structure in this library can serve, in turn, as the origin for a kick. If this procedure is repeated enough times, eventually all isomeric structures for the

molecule will be found. It is hard to see why any specific structure would not eventually be found using this procedure.

How long (how many kicks) will it take to do a complete search? The analysis is similar to that previously described for conformational searches. The time depends on three factors. One is the average time required for an optimization of a kicked structure to reach a minimum. Due to this factor, searches using quantum mechanics will take much more time than molecular mechanics conformational searches. The second factor is the number of minima to be found. This is not known initially; however, as a search proceeds and the rate of appearance of new minima produced decreases one gets a good idea about the total number that might be found. The time required scales as the number of minima. It is important to note that the dimensionality of the structure space is not at all the important factor. It would be if the search method required that one got close to every different point in structure space, but the method described here has no such requirement.

The third factor concerns how sure one wants to be that one has not missed structures. In the case of all conformational and isomeric searches, it is never possible to be absolutely certain that no structures have been missed. However, if one is willing to make some simplifying assumptions, approximate probabilities can be calculated. To summarize the results of a published analysis,^{1b} the chance of finding any particular conformer is about 95% if one can conduct three times as many kicks as there are minima to be found. This probability rises to 99.3% if one conducts five kicks for every minimum and to 99.9% if one goes to seven kicks per minimum. The search method converges surprisingly quickly. The formula for obtaining these results is obtained by assuming that the probability of finding the structure in question is the same as for all the others. This probability actually depends on the multidimensional volume of conformational or structural space in which one can land as a result of the kick and refine down to the structure in question. This volume might be called the catch basin for this minimum. If there is a relatively small volume of conformational or structural space that will lead to a particular minimum, the chances of finding it will be less. Fortunately, the lowest-energy minima (in general the most important) tend to have the largest catch basins and therefore are the easiest to find. For the molecule C_6 studied in this article, one could guess that it might require the order of several hundred kicks to do a reasonably thorough search. Unfortunately, kicks that result in falling back to the kicked structure gain no information and cannot be counted for the purpose of the above analysis.

What level quantum mechanical calculation should be used? The usual answer is the highest level that can be afforded. This is a moving target and has changed considerably over the years. If one made this kind of choice for C_6 one would have to restrict the calculation to only a few structures (perhaps linear and a ring) and would not be able to do a search for other minima that might be interesting or important. To do as many kicks as necessary for a good search, one *must* operate at a level lower than the best possible level for the quantum mechanical calculations. However, if we can locate all of the minima even at a lower level of calculation these minima can be refined at a higher level. Hopefully, they would have the same basic structures that one would find if one could do the search with every point being done at the highest level. This refinement at a higher level is only necessary

for the relatively few minima found and not for all the points considered during the search. This concept is related in spirit to a common procedure in quantum mechanics in doing an optimization at the highest level for which this is practical in a reasonable amount of time. One then takes this optimized structure and does a single-point calculation at a still higher level. One hopes that the minimum at this high level has not moved too far.

The stochastic search method employing molecular mechanics has been used for some time. It has been used to locate conformers of acyclic, monocyclic, and bicyclic hydrocarbons, olefins, and other compounds including peptides. Fairly large structures have been studied to obtain all or almost all the conformers because molecular mechanics calculations are rapid on a modern computer. Quantum mechanical optimization is much slower. For this reason, a quantum mechanical search will be limited in the size of molecules, which can be thoroughly explored until computer power is increased beyond its current level. Nevertheless, there are a number of relatively small molecules and ions where finding all the structures would be desirable. Just as in the case of searching for conformers, one can find all the structures for small systems by inspection. However, once the size becomes larger than a certain number of atoms there is a good chance of missing important structures if one searches by inspection.

The particular case studied in this article was the molecule C_6 . The reason for being interested in C_6 is that it has been found that the fullerene C_{76} on heating for several seconds at 1100° loses six carbons to form C_{70} . A species of composition C_6 might be lost. Of course, six carbons could also be lost as three molecules of C_2 or even two molecules of C_3 . The energies and structures of these species are well known. For C_6 , it is not at all obvious how many minimum energy structures exist and what they are. C_6 structures certainly can have bonds of varying orders and distances between the carbons and a variety of conceivable geometric arrangements. It was therefore chosen as a good case for applying this new search method on the GAUSSIAN energy surface. The focus of this work was to try to locate as many minima as possible rather than to do the highest-level calculation on a few low-energy structures.

Implementation

How should the stochastic search procedure for GAUSSIAN be implemented in practice? Ultimately, one would want a program that would automatically take any initial structure (or the just the formula), kick it, and submit the kicked structure to GAUSSIAN optimization. A library function is required to see whether any structure found has been found previously. These steps can be repeated by the program as many times as desired. However, it was considered to be much simpler to begin with a manual procedure. An extremely simple Fortran program (see the appendix) was written that reads a GAUSSIAN input file and then writes a new file that is identical except that coordinates of the atoms have been kicked. This new file is then submitted to GAUSSIAN² (version W03) program for optimization. This Fortran program can be operated as many times as desired to generate different kicked structures because it uses seeds for the random number generator taken from a clock function. When this has been done enough times, the same program can be run using a different kick size. The

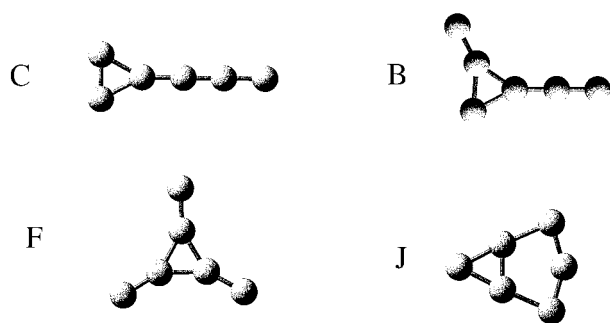


Figure 1. Structures with three rings.

kick size is read from a simple text file. One advantage of doing it this way is that one can see immediately just how the method is operating and take appropriate action if there are problems.

A fully automatic program would need to have a way of recognizing from the GAUSSIAN output whether a newly obtained minimum is the same as any isomer in the library or not. Code could be written to process the distance matrix data, systematically permuting all of the atoms of each type, to accomplish this. However, the library function is extremely easy to accomplish with a manual procedure. The program GaussView produces a picture of any structure obtained by GAUSSIAN whether optimization is complete or not. Simply looking at these pictures tells you when you have a new isomer. One conveniently keeps a set of the GaussView pictures of the different isomers produced for reference.

The controlling parameter in the operation of stochastic searching is the size of the kick. Small kicks will result in return to the kicked isomer. It is easy to start with a small kick and gradually increase it to see when isomerization starts to occur with some reasonable probability. This probability will become larger with further increase of the kick size. What is the problem with using very large kicks? With very large kicks, molecules often break into separate pieces. These pieces do not usually come back together on optimization to form normal bonds and the optimization usually stops at some point. Strictly speaking, one could regard these loose complexes of smaller species as forms of C_6 . However, in this project it was not intended to find and study them and they were ignored. One can easily see whether such fragmentation has occurred from the GaussView picture of the final structure in an optimization. With experience, one can fairly readily find the range of kick size, which gives a reasonable probability of isomerization and yet does not cause fragmentation to occur too frequently. A modified Fortran program was written to decrease the number of times when fragments would be formed. Kicked structures were examined to see if they were likely to separate into two or more pieces. Such kicked structures were rejected and the program automatically performed additional kicks until a structure that was not likely to fragment was produced.

Inline with the discussion above, the basis set restricted Hartree-Fock (RHF)/6-311G was chosen for this study because minimization of a C_6 structure at this level in general takes only a few minutes on a computer with a 2.65-GHz processor. Much better calculations can be readily done with larger basis sets or by

including correlation or with density functional methods. However, using the same amount of computer time one would be forced to stop after fewer kicks. It was felt that it was better to do a more thorough search with a lower-level calculation. The minimum energy structures obtained can later be refined at a higher level. To face the possibility that there might be additional minima on the higher-level surface that do not exist at the lower level, one could supplement the lower-level search by doing a relatively small number of additional kicks on the structures obtained by higher-level calculations and refine them at this level.

Two simple starting structures for C_6 are obvious. One can choose a chain or a ring. A QCLDB literature search for C_6 found more than 50 articles describing calculations using these choices for C_6 . The titles of many of these articles reflect the desire to determine which of (only) these two possibilities was favored. A ring was used here (six-fold symmetry D_{6H}) as the initial structure. It was optimized to give a structure with bond lengths of 1.294 Å. However, frequency calculation indicates that it is a transition state with two imaginary frequencies. It would be simple to move any atom and go downhill. Instead of doing this, a stochastic kick was used. With very small kicks, only a single product was formed. This was a structure of the lower symmetry D_{3h} (Fig. 1). A similar structure has been described many times previously. It has CC bond lengths of 1.315 Å and bond angles of 141.5 and 98.5°. It is a minimum on the 6-311G energy surface and at other levels. There is nothing wrong with having a transition state as the starting point for a search. Even small kicks start the structure going downhill toward a different structure. The only structure discovered in the vicinity of the sixfold symmetrical transition state using small kicks was the planar structure with D_{3h} symmetry. When the kick size was increased to 0.75 Å, new structures started to appear. One is the linear structure with bond lengths of 1.275, 1.292, and 1.287 Å. Kicks have resulted in isomerization breaking a bond of the ring.

Usually, using the stochastic search procedure, one kicks any new structure that has been obtained rather than the original one. The reason for doing this is to try to move over as much of structure space as possible. In this study, the starting sixfold symmetrical structure was explored at length to try to locate any

Table 1. Isomers of C_6 .

	Lowest frequency	Energy	Total dipole moment
D_{3H}	450.75	−226.714340	0.0000
Linear	81.85	−226.784822	0.0000
A	219.59	−226.612641	0.6424
B	131.07	−226.697352	2.4876
C	103.92	−226.719053	1.1105
D	76.92	−226.637555	0.4116
E	146.72	−226.695693	1.0388
F	199.96	−226.684138	0.0000
G	29.36	−226.609087	1.7396
H	242.69	−226.628467	0.0000
I	169.77	−226.550752	1.7527
J	40.06	−226.587697	1.8160
K	198.81	−226.567712	0.7732

minima that might be close to it. Kicking the ring structure opened it to the linear structure frequently, but it also yielded five structures that had not previously been discussed in the literature. Each of these newly found isomers were then kicked systematically with kicks ranging from 0.6–1.0 Å in the next part of the search. Frequently, one isomer went to another. However, three additional new isomers were discovered this way. Eight isomers, in addition to the ring and chain were found in this way. They were labeled A–H. Structure A is unusual. It is the only one of these that is nonplanar. It probably would not have been easy to guess in advance.

It was tempting to believe that the search at the 6-311G level was complete at this stage. Repeated kicks to all the known minima did not lead to any new ones. However, if one notes that all of these structures are planar except for A and D (and they are close to planarity) it might be suggested that the probability of a kick producing a very nonplanar structure from any of these might be very low. How can one deal with this possibility? It would be better if we could start the search without inputting any specific chosen structure. A convenient way was found to do this. A GAUSSIAN input file was written with all six carbons at the origin. When this was kicked with a 1-Å kick parameter, random structures were produced. It was noted that many of them had carbon atoms that were close together. A filter was added to the Fortran program to reject these structures. When files generated in this way were submitted to GAUSSIAN for optimization, it was found that optimization took a much longer time to go to minima than with previous files. When they did eventually go to minima, the first six files produced this way refined to structures already in the library. However, the seventh file yielded new isomer I. Note that isomer I has a cage structure and is far from being planar. Two more “new” structures were found in this way. Clearly, it was valuable to use this “zero” input structure as a means of avoiding biasing the search. Even though kicking from these structures takes more computer time, it is worth doing. It is probably a good way of beginning a search. However, the structures found previous to using it are still minima on the 6-311G surface so it is not necessary to start all over. These three new structures are higher in energy than the ones found first but are interesting and also make the search more complete.

Can one draw any general conclusions about the probability of kicks of a certain size causing isomerization? Consider two isomers where the catch basins share a border in structure space. If the minimum energy point of the first isomer is close to the border while the minimum of the second isomer is far from the border, it is clear that even small kicks will have a reasonable probability of converting the first isomer to the second. The same sized kicks could have zero probability of doing the reverse transformation. Much larger kicks would be necessary to do this. Note that the relative energies of the isomers is not a consideration. The question is whether a kick can geometrically cross the border. Interconversion of a simple ring and the linear structure would probably have this relation. Even modest kicks might be able to separate two atoms of the ring enough so that optimization would proceed downhill to the linear structure. It would take a very much larger kick of the linear structure to get it to close to the ring and even large kicks would have low probabilities of doing this.

Many more kicks of all of the isomers found should be given to further reduce the chance that any other isomers have been missed. A disadvantage of doing this procedure manually is that one gets tired. An automated system would run day and night and would soon do a complete search for the C₆ isomers. What has been demonstrated is that with little effort even the manual stochastic search method locates a substantial number of new isomers on the GAUSSIAN energy surface.

The basic stochastic kick idea can be used with the object of finding all of the minima as it was in this case. However, it would be also be possible to do an intensive search for additional minima in the region of one interesting structure. One would start with small kicks and use larger and larger kicks to locate all of the minima that are structurally similar to the starting structure. There would be many instances where what could be described as a local search of this nature might be useful.

Results and Discussion

Clusters of carbons atoms have been of interest in chemistry for a long time. In a few cases (C₂, C₃, C₆₀, and others) there is detailed structural and energetic information from experiments, but in most cases this is not available. It is necessary to employ theoretical methods to learn about them. There have been many calculations published concerning carbon clusters. For the relatively small cluster C₆ there are over 50 articles but only chain and simple ring structures have been extensively investigated. Jones³ reported searching for C₆ structures with a molecular dynamics approach using quantum mechanics calculation and finding isomers higher in energy than the ring and linear structures but does not give these structures or the details of the method.

It has been demonstrated here using the stochastic isomer search method that (at the 6-311G level) there are 11 additional minima on the energy surface. One of these new structures (C) is better than the linear structure at this level. There might well be a few more that have been missed. Several hundred kicks and optimizations were used to obtain these results.

Examining this set of structures might make it possible to deduce qualitative bonding principles for C₆ clusters. Once discerned, such motifs might well be applicable to larger clusters as well. If one examines the C₆ structures found here, one sees that four of the structures have a common feature. In each of them, there is a ring of three carbons with the other three carbons attached to this ring (Fig. 1). The substituents are simple chains in the plane of the ring. One structure has a single linear three-carbon chain (C). There is another with a two-carbon chain and one carbon attached (B). The third one has three one-carbon substituents (F). Isomer (J) has a three ring with the remaining three carbons bridging adjacent ring atoms.

Arranging the isomers found into families permits one to consider missing members of a family as possible additional isomers that might have been missed by the search. Three of the isomers found may be considered as substituted four-membered rings (Fig. 2). A structure with a two-carbon substituent looks somewhat like a derivative of a planar bicyclobutane (E). Another isomer (D) has a four-carbon ring with single carbon substituents at the 1 and 3 positions. It is slightly nonplanar with a dihedral angle of 10°.

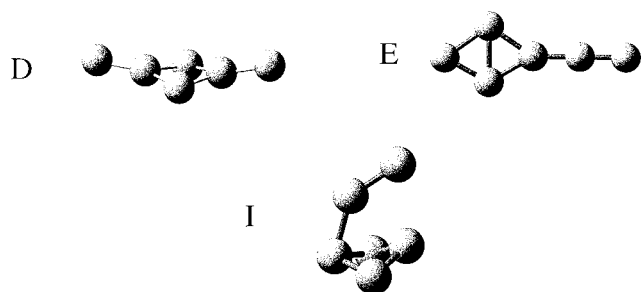


Figure 2. Structures with four rings.

Such a structure naturally suggests considering the corresponding 1, 2 isomer. A structure of this nature was input to see whether such an isomer might have been missed in the search. Optimization did proceed to a stationary point. However, frequency calculation yielded one imaginary frequency, indicating that the structure is a transition state. When it was given a very small kick, a rearrangement occurred to the three-membered ring structure (F), which had been previously found. A detailed pathway for this rearrangement was obtained by following this optimization from the kicked structure. The third isomer (I) has a two-carbon chain almost closing to a bicyclic structure.

The structures found with five-membered rings are peculiar (Fig. 3). In contrast with those containing three- and four-membered rings where the entire structure is planar, one of the five-membered ring species (A) is nonplanar. It also has very different bonding distances around the ring. The other minimum energy structure is related to it, but it is *planar* with one very long ring bond (G). Three minima among those found have six-membered rings, but all are distorted from the six-fold symmetrical structure. One is the D_{3h} mentioned. Another is the D_{2h} structure (H) and the third is (J).

With saturated hydrocarbons, in addition to the straight chain, all branched chain structures are possible as isomers. Even though the straight chain of six carbons is the lowest-energy structure found at the 6-311G level for C_6 , no simple branched chain structure was obtained. In view of the discussion above, it seems likely that any such branched chain would optimize by closing to a ring of lower energy. This idea was tested by adding a one-carbon branch to the linear C_6 structure. Optimization took this C_7 structure directly to an energy minimum with a three-membered ring.

It is likely that doing searches on larger carbon clusters will produce structures that will suggest further structural motifs. So far, there does not seem to be any bonding principle nearly as simple as that which works for saturated and unsaturated hydrocarbons where we have tetrahedral, trigonal, and linear bonding arrangements around each carbon. Carbon clusters might be de-

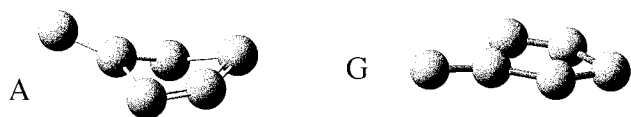


Figure 3. Structures with five rings.

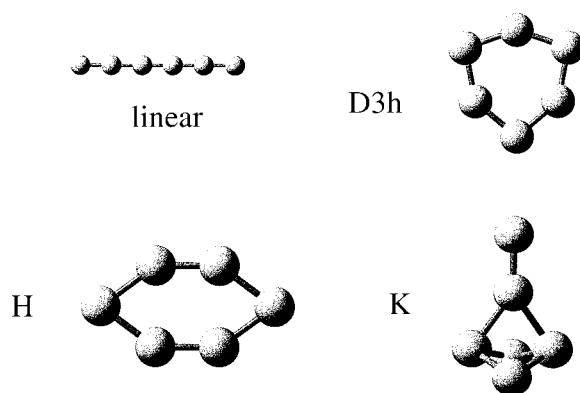


Figure 4. Other structures

scribed as hyperunsaturated hydrocarbons. Once we discover bonding principles for carbon clusters from looking at structures, we may be able to construct (after the fact) arguments that rationalize them in terms of some kinds of orbitals as we do for ordinary hydrocarbons. The other isomers found are shown in Figure 4.

The search reported here has been for singlet structures and at one chosen *ab initio* level. Clearly, a search could also be carried out for C_6 triplets in exactly the same way as in the search for singlets described here. The set of structures obtained is likely to be entirely different. In addition, the same search method might also be applied to find all the isomeric structures for the C_6 cations and anions. These ions can be readily produced and detected using a mass spectrometer, but the structures are not obtained in this way.

Another area where stochastic methodology might be applied involves searching for all the transition states on an energy surface. The same search principle as that used here should work effectively in locating all the transition states. However, a complete search for transition states would probably take much more computer time. There are liable to be many more transition states than minima on a typical surface. In addition, the options available in GAUSSIAN for going toward transition states are liable to operate over smaller catch basins than those for locating minima. It would therefore take many more kicks to find them all. Nevertheless, a procedure for finding all of the transition states should be valuable even if it takes longer.

A local search for transition states might be valuable in a number of cases. One would be looking for the ways in which one particular structure isomerizes. This would be carried out by starting with small kicks. Initially, all kicks would result in return to the kicked structure. If one slowly increases the size of the kick parameter, eventually some kicks should result in isomerization. Structures that isomerize as a result of these minimum kicks might be close to a transition state for the process. Refinement of the kicked structure using an option that seeks a transition state should have a good chance of finding one. It should be pointed out that the minimum sized kick that results in isomerization is that which goes to the closest point in the catch basin of the other isomer. This point is not necessarily at the transition-state geometry or energy.

Acknowledgment

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Appendix

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DIMENSION x(100), y(100), z(100), x1(100),
          y1(100), z1(100)
integer*4 iseed
character*80 a1, name
character*12 fname
character*1 e1 (100)
open (21, file = 'kicksize.tx', status =
  'old')
open (23, file = 'kicked.gjf', status =
  'unknown')
read (21, 21) rad, name
21 format (f10.0, /a)
fname = name
open (22, file = fname, status = 'old')
sec = secnds (73.7)
int1 = sec
int2 = (sec-int1) *10000
int1 = 2* (int1/2) +1
iseed = 2* (int2/2) +1
do 200 i = 1, 7
  read (22, 1) a1
  write (23, 1) a1
1 format (a)
200 continue
no = 6
do 10 i = 1, no
  read (22, 2) e1 (i), izero, xx, x (i), y
    (i), z (i)
2 format (a2, i1, 4f18.0)
10 continue
do 50 i = 1, no
100 dx = rad* (2.*ran (iseed) -1.)

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dy = rad* (2.*ran (iseed) -1.)
dz = rad* (2.*ran (iseed) -1.)
dist = sqrt (dx**2 + dy**2 + dz**2)
if (dist.gt.rad) go to 100
x1 (i) = x (i) + dx
y1 (i) = y (i) + dy
z1 (i) = z (i) + dz
write (23, 16) e1 (i), x1 (i), y1 (i), z1
  (i)
16 format (2x, a2, ', 0, ', 3f12.5)
50 continue
write (23, 51)
51 format (///)
write (23, 23) rad, name
23 format (' kick size = ', f12.2, /a)
STOP
END

```

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