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Recommended Citation

P. L. Plummer and B. N. Hale, "Molecular Model for Prenucleation Water Clusters," *Journal of Chemical Physics*, vol. 56, no. 9, pp. 4329-4336, American Institute of Physics (AIP), May 1972.
The definitive version is available at https://doi.org/10.1063/1.1677867

Molecular Model for Prenucleation Water Clusters*

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(Received 10 December 1971)

A molecular model applicable to prenucleation water clusters is described. As an illustration the model is applied to water clusters having clathrate-like structures composed of five-membered rings. This work was motivated by the apparent inadequacies of the corrected liquid drop model which (in addition to applying bulk properties to small clusters) predicts nucleation rates which may be as much as 10^{17} larger than experiment. We present the "energy of formation" at a temperature of 277°K for our molecular model for clusters ranging in size from 5 to 57 molecules. These results agree qualitatively with experiment and, we believe, provide a motivation for further development of the molecular approach.

I. INTRODUCTION

We present a molecular model for prenucleation water clusters which has specific application to the homogeneous nucleation of water from a supersaturated vapor. In a calculation of the steady-state nucleation rate it is necessary to know the quasiequilibrium size distribution of water clusters in the supersaturated system.[1] In the past this size distribution has been approximated assuming the *classical model*, i.e., that the water clusters are spherical liquid drops[2,3] with bulk properties such as surface area and surface tension. The size distribution requires the determination of $\Delta\phi^0(g)$, the standard change in Gibbs free energy accompanying the formation of a cluster with g molecules from g monomers in the supersaturated vapor at the temperature, T. In the classical model $\Delta\phi^0(g)$ is given by[2]

$$\Delta\phi^0(g) = 4\pi r_0^2 \sigma - gkT \ln S, \qquad (1)$$

where σ is the surface energy per unit area, r_0 is the radius of the g cluster, and S is the supersaturation. Once $\Delta\phi^0(g)$ is known the size distribution is obtained from

$$N(g) = N_0(1) \exp[-\Delta\phi^0(g)/kT], \qquad (2)$$

where $N(g)$ is the number of clusters with g molecules, and $N_0(1)$ is the equilibrium number of monomers.

For many years this classical model has predicted nucleation rates which are roughly the correct order of magnitude and has given reasonable agreement with critical supersaturation measurements.[4,5] However, in 1962 Lothe and Pound[6] reopened a question originally noted by Kuhrt[7] and later by Frenkel[2] concerning terms missing from this so-called *free energy of formation* of the g cluster. The expression given in Eq. (1) accounts for bulk energy and surface energy of the cluster but does not include the energy of translation and rotation of the center of mass. When this energy is included the size distribution is increased by approximately 10^{17} and for the condensation of water vapor the quantitative agreement with nucleation rate experiments is destroyed.[8] However in modifying Eq. (1) the matter is not as simple as adding the translational-rotational energy. One must also account for the energy available

from the deactivation of six degrees of freedom in the bulk.[9] This additional term has been called the *replacement* term[6] and it is on its estimation that current controversies center.

The classical model has many merits. It avoids the formidable problem of treating each cluster on a molecular basis and relates the free energy of formation to measurable bulk properties. However these properties such as surface tension and surface area have a questionable interpretation for clusters with less than 100 molecules and in addition one faces conceptual difficulties with the corrected classical model because of the inability to uniquely relate terms in the statistical model to terms in the classical model. These difficulties could be avoided by a *complete* statistical mechanical treatment. However the complete treatment requires a realistic potential for the cluster-vapor system. A modification of this approach has been attempted for argon clusters using a Lennard-Jones potential.[10] But in the case of water a realistic intermolecular potential which can be applied to an arbitrary number of water molecules is not available[11] and would in any case be impractical for use with large clusters.

Our approach has been to take *advantage* of just those properties of the water molecule which make its intermolecular potential so difficult to handle. That is, we assume a relatively strong hydrogen bond ($\sim 10kT$ at room temperature) and impose what we feel to be reasonable criteria for a cluster structure *model*. Cluster models[12] are constructed which (1) maintain nearly tetrahedral angles between hydrogen bonds, (2) maximize the number of bonds, and (3) require the highest degree of spherical symmetry for the cluster as a whole. These models are then used to approximate the cluster partition function and finally the energy of formation of the cluster and the cluster size distribution. In this paper we report our results assuming closed and partially closed clathrate structures composed of five-membered rings ranging in size from 5 to 57 molecules.

Except for satisfying the criteria stated previously, the clusters we have chosen are arbitrary and they are not claimed to exist in the supersaturated vapor. Furthermore the cluster structures considered are necessarily limited in number and as such could not com-
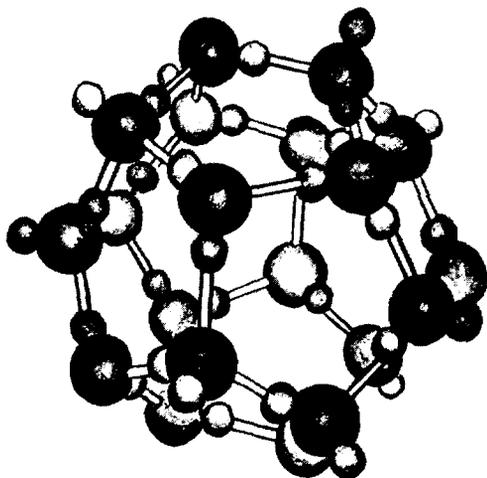
FIG. 1. Twenty molecule single cage structure.

pletely describe the supersaturated vapor system. However we feel that this constitutes a first step in an approach which incorporates characteristic properties of the water molecule explicitly without sacrificing the feasibility of a solution. As such it offers an alternative midway between treating 5–100 molecule water clusters as liquid drops and the nearly impossible complete molecular treatment. A number of approximations have been made in our evaluation of $\Delta\phi$ and we view this work as an indication of the possibilities of such an approach rather than as a rigorous determination of $\Delta\phi$.

II. FORMALISM

A. The Size Distribution

We use a statistical mechanical expression for the size distribution based on the traditional assumption that the supersaturated vapor system consists of a mixture of noninteracting ideal gases. Each collection of clusters with g molecules is assumed to be an ideal gas of indistinguishable particles. The grand partition function Ξ for this system is the product of grand partition functions for the component gases, $\Xi(g)$, and is given by

$$\Xi = \prod_g \sum_{N(g)} \exp[N(g)\mu(g)/kT]Z[N(g)], \qquad (3)$$

where $N(g)$ is the number of clusters of size g and $Z[N(g)]$ is the canonical partition function for the gas of g clusters. Since

$$Z[N(g)] = Z(g)^{N(g)}/N(g)! \qquad (4)$$

and

$$N(g) = kT\partial \ln\Xi/\partial\mu(g) \qquad (5)$$

one obtains

$$N(g) = \exp[\mu(g)/kT]Z(g); \qquad (6)$$

$Z(g)$ is the partition function for the g cluster. With $\mu(g) = g\mu(1)$ [13] one arrives at the standard result:

$$N(g) = [N(1)/Z(1)]^g Z(g). \qquad (7)$$

This can be written in the form

$$N(g) = N_0(1) \exp\{-\Delta\phi(g)/kT\}, \qquad (8)$$

where

$$\Delta\phi(g) = -kT \ln[Z(g)/N_0(1)]$$
$$+ gkT \ln[Z(1)/N_0(1)] - gkT \ln S. \qquad (9)$$

The supersaturation, S, is $N(1)/N_0(1) = P/P_0$. P is the vapor pressure in the supersaturated system and $N_0(1)$ is the equilibrium number of monomers at the temperature T (and equilibrium vapor pressure, P_0). In analogy with Eq. (1) we refer to $\Delta\phi(g)$ in Eq. (9), as the "energy of formation" of the g cluster. The problem thus reduces to evaluating the partition functions, $Z(g)$, for our choice of cluster structures.

B. The Cluster Model

It is not known whether aggregates of water molecules such as the prenucleation clusters have well-defined, preferential structure or whether no structure exists beyond nearest neighbors. However since local structure appears to be retained in liquid water,[11] (where densities and collision rates are high) it is reasonable to consider that structure plays some role in precondensation nuclei (where the collision rates are lower and a structure once formed, may have a longer lifetime). However, the clusters in the supersaturated vapor do grow and disperse at least partially upon collisions with the carrier gas and vapor molecules; and internal vibrations excited by previous collisions can result in spontaneous emission of molecules from the cluster. Therefore, if we are to assume that the cluster structure is meaningful, we must assume (1) that the lifetime of a given cluster structure is sufficiently long that its internal vibrational spectrum can be characterized and (2) that the supersaturated vapor system can be described on the average as a quasiequilibrium distribution of water cluster structures. In the case of water the geometry and strength of the hydrogen bond are the major driving forces for cluster formation. Since the hydrogen bond energy is about $10kT$ this appears to be a reasonable assumption. The cluster internal normal mode oscillations in our calculations have a maximum period of about 10^{-11} sec; this is appreciably shorter than the time between collisions (10^{-7} sec at 1 atm). Thus our assumption of a well-characterized internal vibration spectrum appears justified as long as the cluster is relatively stable between collisions.

The clathrate structure proposed by Pauling[14] is a particularly favorable model both from the standpoint of energetics and symmetry and fulfills the criteria set
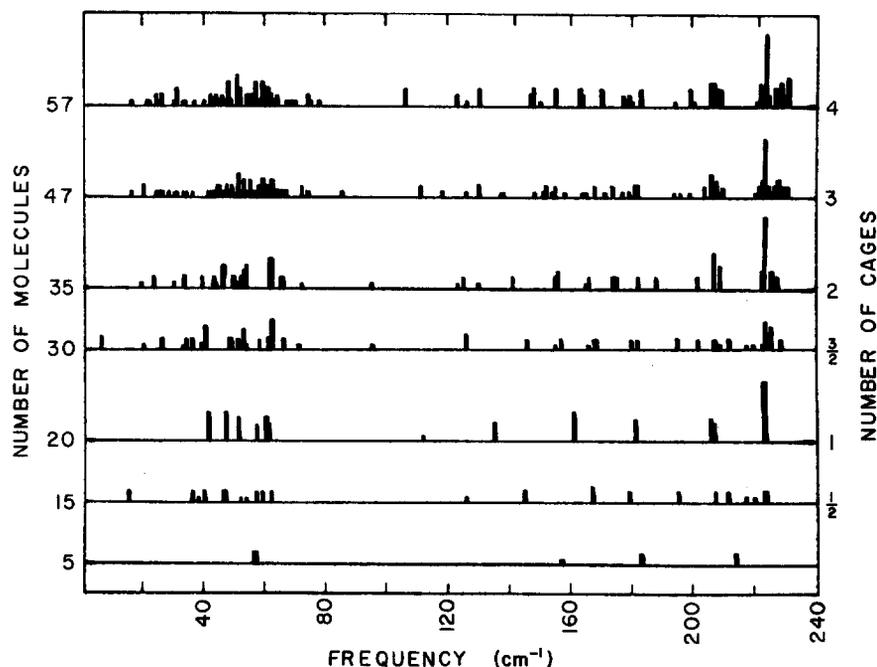
FIG. 2. Normal mode frequency spectrum for representative clusters. The height of the lines represents the number of modes per unit frequency interval.

forth in Sec. I. Furthermore the extension of this model to several cages provides considerably more symmetry than an ice-like lattice. However the perfectly ordered clathrate structures adopted here cannot be extended indefinitely in size. They exhibit considerable strain as the number of molecules exceeds 80. Beyond this size it becomes difficult to maintain the closed cages without grossly distorting the bond angles and bond lengths. Therefore as a first step in the analysis of specific cluster structures we have limited our study to small clusters composed of pentagonal rings and specifically to those consisting of 5, 8, 10, 12, 15, 17, 20, 27, 30, 35, 39, 40, 41, 45, 47, 50, and 57 water molecules. The 20 cluster structure is shown in Fig. 1.

C. The Partition Functions

We assume the following form for $Z(g)$, the cluster partition function:

$$Z(g) = Z_t(g)Z_r(g)Z_I(g), \qquad (10)$$

where

$$Z_I(g) = Z_v(g) \exp[-E_B(g)/kT]. \qquad (11)$$

$Z_v(g)$ is the vibrational partition function and $E_B(g)$ is the g cluster binding energy. The translational partition function, $Z_t(g)$, is that of a body of mass gm (where m is the mass of a water molecule) in a volume V and is given by

$$Z_t(g) = V(2\pi mgkT/h^2)^{3/2}. \qquad (12)$$

Assuming a rigid cluster, the rotational partition func-

tion, $Z_r(g)$, is

$$Z_r(g) = \pi^{1/2}(8\pi^2 kT/h^2)^{3/2}(I_1 I_2 I_3)^{1/2}/\delta \qquad (13)$$

The principal moments of inertia, I_1, I_2 and I_3 are obtained by treating the component water molecules as point masses in the cluster; δ is the symmetry number corresponding to the number of physically indistinguishable rotational orientations.

Implicit in Eq. (11) is the assumption that the cluster can support vibrations about some equilibrium configuration. For these calculations we have assumed only one structure for each g sized cluster. To find the normal mode vibrations one should assign a set of generalized coordinates representing the displacement of *every atom* in the assumed cluster structure from its equilibrium position, and (since the potential is unknown) choose a set of force constants corresponding to all internal motions. Such a program is not reasonable for large clusters since it requires a disturbing number of arbitrarily assigned force constants. In addition, it is impractical since the potential energy matrix rapidly becomes too large for diagonalization with available computer facilities. In the interest of feasibility we assume that the $(3g-6)$ intermolecular vibrations, the $3g$ intramolecular vibrations and the $3g$ molecular librations are decoupled and that each can be described by normal mode oscillations about their respective equilibrium positions. This approximation is consistent with the wide separation in the characteristic frequencies each of which can be essentially attributed to one of these types of molecular motion. With this assumption $Z_v(g)$ can be factored into the intramolecular, the librational, and the intermolecular vibrational con-

TABLE I. The intramolecular and librational frequencies.

Intramolecular[a] frequencies (cm^{-1})

$\nu_{11}=3695$	$\nu_{12}=3545$	$\nu_{13}=1645$
$\nu_{21}=3690$	$\nu_{22}=3555$	$\nu_{23}=1650$
$\nu_{31}=3565$	$\nu_{32}=3470$	$\nu_{33}=1655$
$\nu_{41}=3565$	$\nu_{42}=3470$	$\nu_{43}=1655$

Librational frequencies (cm^{-1})

$\nu_{51}=384$	$\nu_{52}=480$	$\nu_{53}=624$
$\nu_{61}=312$	$\nu_{62}=464$	$\nu_{63}=600$
$\nu_{71}=384$	$\nu_{72}=480$	$\nu_{73}=536$
$\nu_{81}=456$	$\nu_{82}=512$	$\nu_{83}=608$

[a] The first index indicates the number of bonds.

tributions:

$$Z_v(g)=Z_{intra}(g)Z_{libr}(g)Z_{inter}(g). \quad (14)$$

The normal mode frequencies for $Z_{inter}(g)$ are calculated directly by assuming that the water molecules are point masses and that the potential energy may be written

$$U=U_0+\tfrac{1}{2}K_r\sum_{i,j}\Delta r_{ij}^2+\tfrac{1}{2}K_\alpha\sum_{i,j,k}\Delta\alpha_{ijk}^2, \quad (15)$$

where Δr_{ij} is the change in bond length between molecules i and j and $\Delta\alpha_{ijk}$ is the change in angle between the molecules i, j, and k; K_r and K_α are the corresponding force constants. U_0 contains all other functional dependence of the potential energy which, to be consistent with the stated assumptions, will depend on the equilibrium positions of all the atoms and (quadratically) on the small displacements of the atoms within each water molecule in the cluster. U_0, by assumption, contains no coupling between those coordinates describing the intramolecular, intermolecular and librational motions. For K_r we use 0.19×10^5 dyn/cm and for K_α we use 0.0362×10^5 dyn/cm,[15] approximately the force constants for ice.[16] The resulting intermolecular normal mode frequencies are in the range 20–240 cm^{-1}. Figure 2 shows these frequencies for seven representative clusters.

The intramolecular and librational frequencies were estimated in the following way. For a cluster of g molecules[17] we adopt the prescription:

$$Z_{intra}(g)=(Z_1)^{N_1}(Z_2)^{N_2}(Z_3)^{N_3}(Z_4)^{N_4}, \quad (16)$$

$$Z_{libr}(g)=(Z_5)^{N_1}(Z_6)^{N_2}(Z_7)^{N_3}(Z_8)^{N_4}, \quad (17)$$

where Ni is the number of molecules participating in i bonds and

$$Z_i=\prod_{j=1,3}\frac{\exp(-ch\nu_{ij}/2kT)}{1-\exp(-ch\nu_{ij}/kT)}. \quad (18)$$

The ν_{ij} are given in Table I. The intramolecular frequencies, ν_{1j}–ν_{4j}, for the different bonding configura-

tions were determined in a separate calculation on small clusters in which all the hydrogens were included. The dimer frequencies were made to fit with experimental results[18] by adjusting the force constants. These force constants were subsequently used to calculate the frequencies for the trimer and tetramer. The dimer frequencies were then assigned to one-bonded molecules, the frequencies unique to the trimer to two-bonded molecules, etc. The frequencies for three and four bonded molecules were taken to be the same. The librational frequencies were estimated from experimental data[19] of water adsorbed in crystals. In each case the frequencies used were those associated with water in an environment most closely approximating that in the proposed structures, i.e., those participating in one to four bonds with appropriate symmetry. These librational frequencies are probably accurate to within 20% and were used in the absence of direct calculations or more applicable data.

The total binding energy for the g cluster, was approximated as

$$E_B(g)=(N_1/2)E_1+N_2E_2+(3N_3/2)E_3+2N_4E_4, \quad (19)$$

where E_i is an estimate of the dissociation energy of the ith bond. For these calculations $E_1=6.10$ kcal/mole, $E_2=6.28$ kcal/mole, $E_3=6.36$ kcal/mole, and $E_4=6.40$ kcal/mole. These estimates were taken from INDO[20] type calculations on small clusters containing two to five water molecules.[21] The geometries used in these bond energy calculations approximated those found in the proposed cluster structures.
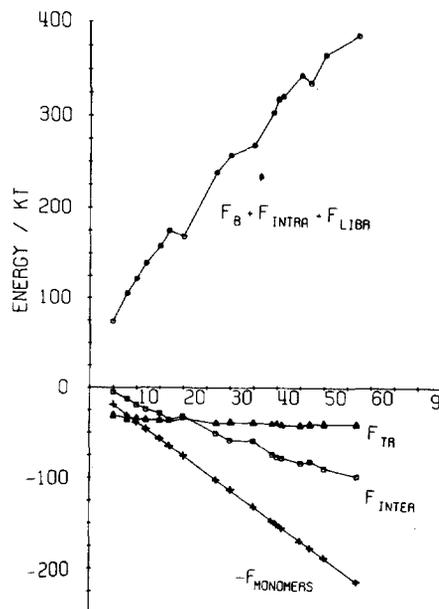

FIG. 3. Contribution to $\Delta\phi$ of various terms as a function of cluster size g.

III. RESULTS AND CONCLUSIONS

In summary the "energy of formation" for the molecular model is defined as

$$\Delta\phi(g)/kT \equiv [F_{\text{inter}}(g) + F_{\text{TR}}(g) + F_{\text{intra}}(g) + F_{\text{libr}}(g)$$

$$+ F_B(g)] - g[F_{\text{TR}}(1) + F_{\text{intra}}(1) - \ln S]$$

$$= F(g) - gF(1), \qquad (20)$$

where

$$F_\alpha(g) \equiv -\ln Z_\alpha(g) \quad \text{and} \quad F_B \equiv E_B/kT.$$

Fig. 3 illustrates the contribution of some of the terms in Eq. (20) to the total energy of formation. The major structural dependent features are reflected in the terms F_{inter} and F_B. Structures with completed cages, e.g., $g = 20, 35, 47$, and 57, have larger binding energies than other clusters of comparable size. Furthermore, these completed structures do not exhibit the low normal mode frequencies characteristic of the open structures; hence $|F_{\text{inter}}|$ for the completed cages is smaller than for open structures with approximately the same number of molecules.

Since our intent was to consider only the most stable structure for a given sized cluster, the more open geometries were excluded from this study. An extensive study which would include all sized clusters, constructed of partial as well as completed five membered rings, would yield a vast number of clusters with higher energies of formation than the majority presented here. These open structures would have increased numbers of one or two bonded molecules and could thus support lower frequency normal mode oscillations. An even more important effect is the reduction in binding energy exhibited by the open structures. The latter results from a decrease in the number of bonds per molecule and hence in a reduced strength of the average bond.

The results for the total energy of formation are shown in Fig. 4 for $S = 5$ and a temperature of 277°K. As would be expected from our model, the energy of formation is not a smooth curve but displays maxima and minima characteristic of the varying stability of the clusters. The solid line is the classical free energy as calculated from Eq. (1). Agreement with the classical result is satisfactory for a range of temperatures around the freezing temperature. However, we should point out that the temperature dependence of the molecular model differs from that of the liquid drop model. In the molecular model the energy of formation *increases* with increasing temperature, whereas the opposite is true in the liquid drop model. The variance of the energy of formation with temperature and critical supersaturation is the subject of additional studies now in progress. We note that the temperature dependence exhibited by our molecular model is similar to that obtained in the study of argon clusters.[10]

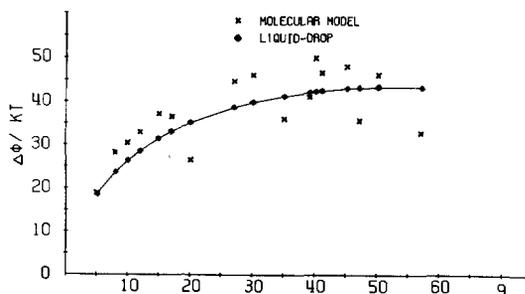We consider the agreement of our model with the

FIG. 4. Energy of formation as determined by the classical and molecular models for g-sized clusters.

uncorrected classical free energy of formation (see Fig. 4) and hence with experiment quite surprising—particularly in view of the approximations involved. However the results would be sensitive to small changes in binding energies and librational frequencies and we prefer to view these results as incentive for further pursuits of cluster structure rather than as a successful prediction for $\Delta\phi$. Other structures including the ices are being investigated. Our preliminary results on ice I indicate that these structures have a higher energy of formation than clathrate structures of similar size. In conclusion we feel that the results of our molecular model convincingly display that an alternative to the liquid drop model exists and merits further study.

ACKNOWLEDGMENTS

* Work supported in part by the Atmospheric Science Section, National Science Foundation, GA 32386.

[1] *Nucleation*, edited by A. C. Zettlemoyer (Dekker, New York, 1969).

[2] J. Frenkel, *Kinetic Theory of Liquids* (Dover, New York, 1955).

[3] L. Farkas, Z. Physik. Chem. (Leipzig) **125**, 236 (1927); M. Volmer and A. Weber, *ibid.* **119**, 277 (1926); R. Becker and W. Doering, Ann. Physik. **24**, 719 (1935); J. B. Zeldovitch, J. Expt. Theoret. Phys. **12**, 525 (1942); Acta. Phys. Chem. URSS **18**, 1 (1943).

[4] M. Volmer and H. Flood, Z. Physik. Chem. (Leipzig) **170**, 273 (1934); J. Feder, K. C. Russell, J. Lothe, and G. M. Pound, Advan. Phys. **15**, 111 (1966); C. T. R. Wilson, Phil. Trans. Roy. Soc. London **A189**, 265 (1897); C. F. Powell, Proc. Roy. Soc. (London) **A119**, 553 (1928).

[5] Jens Lothe and G. M. Pound, *Nucleation*, edited by A. C. Zettlemoyer (Dekker, New York, 1969), Chap. 3, p. 119–120.

[6] Jens Lothe and G. M. Pound, J. Chem. Phys. **36**, 2080 (1962).

[7] F. Kuhrt, Z. Phys. **131**, 185 (1952).

[8] L. B. Allen and J. L. Kassner, Jr., J. Colloid and Interface Sci. **30**, 81 (1968).

[9] This reasoning stems from the standard method of estimating $\Delta\phi^0$ which evaluates the difference between the chemical potential of g molecules in the bulk $(g\mu_B)$ and the chemical potential of the g cluster, $\mu(g)$.

[10] J. J. Burton, Chem. Phys. Letters **3**, 594 (1969); **7**, 547 (1970); J. Chem. Phys. **52**, 345 (1970); Surface Sci. **26**, 1 (1971); F. F. Abraham and J. V. Dave, Chem. Phys. Letters **8**, 351

(1971); D. McGinty, J. Chem. Phys. **55**, 580 (1971); K. Nishioka, R. Shawyer, A. Bienenstock, and G. M. Pound *ibid*. **55**, 5082 (1971).

[11] F. H. Stillinger, J. Phys. Chem. **74**, 3677 (1970); A. H. Narten and H. A. Levy, J. Chem. Phys. **55**, 2263 (1971); A. Ben-Naim and F. H. Stillinger, Jr., *Structure and Processes in Water and Aqueous Solutions*, edited by R. A. Horne (Wiley, New York, 1971).

[12] Kassner originally proposed such a cluster structure model and initiated studies of clathrate-like structures. J. L. Kassner, Jr., P. L. M. Plummer, B. N. Hale, and A. H. Bierman, published in *Proceedings of the International Weather Modification Conference*, Canberra, Australia (1971); R. W. Bolander, J. L. Kassner, Jr. and J. T. Zung, J. Chem. Phys. **50**, 4402 (1969).

[13] This result can be obtained from a minimization of the Helmholtz free energy of the vapor system.

[14] L. Pauling, *Nature of the Chemical Bond* (Cornell U. P., 1962).

[15] $K_a \equiv K_a' r_e^2$ where r_e is the equilibrium bond length and $K_a' = K_r/40$.

[16] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford, New York, 1969); N. H. Fletcher, *The Chemical Physics of Ice* (Cambridge U. P., 1970).

[17] Since for the monomer, $g = 1$, no librational or intermolecular modes exist, $Z_v(1) = Z_{\text{intra}}(1)$. The intramolecular frequencies used were 3750, 3650, and 1590 cm^{-1}.

[18] A. J. Jursi and E. R. Nixon, J. Chem. Phys. **52**, 1521 (1970).

[19] H. Boutin, G. J. Safford and H. R. Danner, J. Chem. Phys. **40**, 2670 (1964); L. J. Basile, D. Gronert, and J. R. Ferraro, *Solvent Extraction Research*, edited by A. S. Kertes and Y. Marcus (Wiley, New York, 1969).

[20] J. A. Pople, D. L. Beverage, and P. A. Dobosh, J. Chem. Phys. **47**, 2026 (1967).

[21] P. L. M. Plummer (unpublished results).

Unitary Transformations and Pair Energies. III. Relation to Perturbation Theory

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(Received 22 November 1971)

The effect of unitary transformations among the occupied orbitals of the beryllium atom is discussed. It is shown that pair–pair interaction energies become large for choices other than the canonical Roothaan–Hartree–Fock orbitals. The many-body perturbation theory diagrams responsible for these effects are discussed.

In the first two papers in this series[1,2] we have investigated the effect of unitary transformations among the occupied Roothaan self-consistent-field (SCF) orbitals on the independent-electron-pair estimate of the correlation energy of LiH and BH. Similar results have also been reported for neon.[3] No explanation was offered in these previous papers for the results obtained. In this paper similar results are reported for the beryllium atom along with a theoretical discussion of their meaning.

If a decomposition of the correlation energy similar to that employed by Nesbet[4] and Sinanoğlu[5] is used, energy increments for a sequence of wavefunctions are computed. If the wavefunctions employ nested subsets of configurations, the importance of various types of configurations may be judged. In this paper the energy increments were considered for the beryllium atom. If ϕ_0 is the SCF wavefunction, $\phi_i{}^a$ is an L, S eigenfunction formed from the replacement of orbital "i" by orbital "a," $\phi_{ij}{}^{ab}$ is an L, S eigenfunction formed from the replacement of "i" and "j" by "a" and "b," etc. (notice that i refers to space orbitals and not spin orbitals), then

$$\psi_0 = \phi_0,$$

$$\psi_i = \phi_0 + \sum_a c_i{}^a \phi_i{}^a \qquad (i = 1s, 2s),$$

$$\psi_{ij} = \phi_0 + \sum_{ab} c_{ij}{}^{ab} \phi_{ij}{}^{ab} \qquad (i, j = 1s \text{ or } 2s),$$

$$\psi_{ij}' = \phi_0 + \sum_{ab} c_{ij}{}^{ab} \phi_{ij}{}^{ab} + \sum_a (c_i{}^a \phi_i{}^a + c_j{}^a \phi_j{}^a),$$

$$\psi_{iik}' = \phi_0 + \sum_{ab} (c_{ii}{}^{ab} \phi_{ii}{}^{ab} + c_{ik}{}^{ab} \phi_{ik}{}^{ab}) + \sum_{abc} c_{iik}{}^{abc} \phi_{iik}{}^{abc},$$

$$\psi_{ij-kl} = \phi_0 + \sum_{ab} (c_{ij}{}^{ab} \phi_{ij}{}^{ab} + c_{kl}{}^{ab} \phi_{kl}{}^{ab}),$$

$$\psi_{iijj} = \phi_0 + \sum_{ab} (c_{ii}{}^{ab} \phi_{ii}{}^{ab} + c_{jj}{}^{ab} \phi_{jj}{}^{ab} + c_{ij}{}^{ab} \phi_{ij}{}^{ab}),$$

$$\psi_{iijj}' = \phi_0 + \sum_{\lambda \mu \epsilon \{iij j\}} \sum_{ab} c_{\lambda \mu}{}^{ab} \phi_{\lambda \mu}{}^{ab} + \sum_{abcd} c_{iijj}{}^{abcd} \phi_{iijj}{}^{abcd}.$$

From the energies associated with each of these variational wavefunctions, E_0, E_i, E_{ij}, etc., one can form