

On the use of Laplace's equation for global predictions of internuclear separation and dissociation energy

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Properties of target species can be estimated by various means including interpolations in periodic charts. Interpolation is equivalent to numerical solution of the Laplace equation. A test of this equivalence, within some confidence level, for any N -atomic molecule surrounded by $4N$ nearest neighbors: the sum of the second differences of the data in all directions must be zero. Since very few molecules have $4N$ neighbors with known data, the test becomes: the sum of the averages of the second differences must be zero. The validity of these tests is explored. For radii of main-group atoms, and for internuclear separations of their diatomic combinations, the averages are different from zero and the sums of the averages are zero to within one σ if second-nearest neighbors are used. Dissociation potentials pass the tests but with larger scatter. Predictions for dissociation potentials, using iterative interpolation within boundaries on which there are known data, are reviewed.

KEY WORDS: Laplace equation, internuclear distance, dissociation potential, periodic systems, diatomic molecules

1. Introduction

1.1. The need for data and methods to obtain them

It is difficult to overstate the need which exists for data relative to various molecular properties. The standard methods for obtaining this information are experiment and *ab initio* quantum computation. Both of these methods are expensive and time-consuming to the extent that procedures for the approximate forecasting of data have become very important. One such procedure is to classify molecular species using topological indices describing molecular structures (mathematical chemistry) and to relate these indices to properties of the molecules (QSPR, quantitative structure–properties relationships). Related to these are the constructions of immense property data bases and the use of combinatorial chemistries.

Another procedure is to search for trends among tabulated data for species along one or more axes of an appropriate periodic system of molecules [1–5], e.g., for trends among isovalent molecules. Then, having found a trend by graphical study [6], least squares fitting [7], or the training of neural networks [8], there can follow the prediction of data for the target molecule(s); typically, this method is used for molecules with

few atoms. After many failed smoothings of dissociation energies of selected diatomic molecules at this laboratory, a last-resource step was to solve Laplace's partial differential equation for the periodic-system locations where the target molecules lie, using given data on the boundary surrounding them. The results were surprisingly good. This surprise led to the present study concerning whatever a theoretical basis might exist for using Laplace's equation in the prediction of molecular data, and, if so, what errors will accrue.

This investigation of Laplace's equation as a global predictive tool is foreign to the worldview of quantum chemistry, and indeed, it will no longer be relevant when Schrödinger's equation has been applied to all species. The same is true of all methods for mining molecular data.

1.2. Theoretical aspects presented in this paper

This paper begins with a definition of the periodic systems for the elements and for molecules. Then it refers to use of the triad principle in periodic systems, and to the proof that for one species averaging over row(s) and column(s) is equivalent to a local solution of the discretized Laplace equation. This equation states that the sum of the second differences of the data, over all periodic system directions, will be zero. The paper goes on to describe a test that can be used for molecular properties, the data for which are so sparse that there may be no molecule for which the sum of the second differences can be found. This proposed test consists of averaging the second differences of the data separately along each axis, and determining if the sum is zero. The validity of this test is investigated, and the possibilities that data for both atoms and molecules can satisfy Laplace equation, for one or more properties, are explored.

1.3. Possible uses of the investigation

The practical application of the concept can be illustrated with a hypothetical example, illustrated in figure 1. Suppose that data for some property of BeP, MgP, and

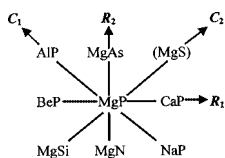


Figure 1. The four axes of the periodic system of diatomic molecules, showing the molecules discussed in the text. Moving from NaP (lower right) to AlP (upper left) involves changing the group number for the first atom from Na to Al. The axes are represented with abandonment of orthogonality, so progression along the R_1 and R_2 axes is restricted to the lines through MgP. The data for some property of all but one species are assumed known, and it is desired to estimate the datum for MgS. It is assumed that the data for this property have been shown on average to follow Laplace's equation. So, if the second differences for the data are positive along the row axes, and if the second difference is negative along the C_1 axis, then it follows that the second difference is also negative along the C_2 axis. This information allows an improved estimate of the datum for MgS from the known data for MgSi and MgP.

CaP; and MgN (MgP again), and MgAs; and NaP (MgP again) and AlP are known. It is then possible to determine the second differences of the data with respect to the *period* number of the first atoms (in group 2 of the periodic chart) and the second atoms (in group 5) of the molecules, and with respect to the *group* number of the first atoms (in period 3), respectively. Assuming that the sums of the second differences have passed the test of being (on average) zero, then the second difference of the data with respect to the group number of the second atoms (from period 3) will be known. Finally, if the datum is known for MgSi, then the hypothetically unknown value for MgS can be estimated from the second difference of the triad MgSi, MgP, and MgS. This estimate should be more accurate than that from a simple triad extrapolation from MgSi and MgP toward MgS.

A variant of this payoff concerns the prediction of data for vast numbers of species simultaneously. If there are known values for a property on some complete boundary of the periodic system, then it must be possible simultaneously (i.e., iteratively) to do triad averages, using all axes of the periodic system, for all the molecules inside the boundary. Some predictions already made will illustrate the levels of accuracy (unexpectedly good) and precision (large) to be expected; these are presented in section 4.

1.4. Definitions

This paper concerns main-group elements, and neutral ground-state molecules formed from atoms of those elements, all in the gas phase. The periods of the elements are 2–6; the groups are 1–7 (though the IUPAC notation 1, 2, and 13–17 are used in the tables). The term “descriptor” refers to atomic charge, electron counts, formula indices such as n in C_nH_{2n+2} , etc. The term “property” refers to such observables as internuclear separation.

2. Theory

2.1. Periodic systems of atoms and molecules

The common charts of the elements are embedded in a chemical space with a period (row) axis R and a group (column) axis C . The most general periodic system of diatomic molecules exists in a chemical space with coordinates R_1 , C_1 , R_2 and C_2 [3,4]. It is a four-dimensional matrix whose elements are molecular symbols, just as the chart of the elements can be represented as a two-dimensional matrix whose elements are atomic symbols. This general system is the outer direct product, of the chart of the elements, with itself. It is a “physical” periodic system, which means that all possible molecules with a given number of atoms are or can be included. Species symbols are multiplicative; thus, the molecular symbol NaCl can be considered formally as the product of the atomic symbols Na and Cl.

Some descriptors are additive in going from atoms to molecules, e.g., atomic numbers. Some properties are approximately additive: e.g., covalent radii r_c and internuclear

separations r_c [9]. For example, the r_c of F and Br are 0.709 Å and 1.142 Å [9] and r_c for BrF is 1.76 Å [10]. Some important cross-sections are likewise additive [11]. If data for these properties are introduced as antilogarithms in the compartments of the chart of the elements, then the diatomic-molecular data will be exponents in the compartments of the periodic system of those molecules.

2.2. The triad principle and the chart of the elements

The triad principle states that the value of some property of an element can be estimated by averaging the values of the species to the left and right in their chart, or the species above and below, or for present purposes both. Mendeleev used the principle to predict properties of Ga, Ge, and Sc (though it appears that his published values were the result of great chemical intuition as much as of arithmetic) [12].

The triad principle continues to attract interest. Zagoryuiko and Zagoryuiko [13] used a global iterative process that included diagonal nearest neighbors in the averages. Given some atomic properties (with which atomic numbers were associated), and leaving blank eight compartments in the chart of the elements (with elements up to number 54), their computer program correctly placed all of the missing atomic numbers [13]. Gorban, Miirkos, and Svitin identified members of periodic-chart groups by plotting properties on atomic number and locating sets of points that can be connected (to within small error) by straight lines [14]. Foyas reproduced most of the periodic chart by subjecting atomic data to self-associative neural-network analysis [15].

2.3. The triad principle, the chart of the elements, and Laplace's equation

An astonishing link exists between the triad principle and one of the most important equations in physics, Laplace's equation, used in such diverse fields as electrodynamics, steady-state temperature distributions, and laminar-flow hydrodynamics:

$$\frac{\partial^2 P}{\partial R^2} + \frac{\partial^2 P}{\partial C^2} = 0, \quad (1)$$

where P is any property and where R and C are the period and group coordinates of the atomic chart. The link is actually to the *discretized* form of the equation,

$$\frac{\Delta^2 P}{\Delta R^2} + \frac{\Delta^2 P}{\Delta C^2} = 0, \quad (2)$$

where ΔR and ΔC are unity for neighboring atoms [16]. Both directions must be used to avoid a trivial result. It follows [16] that if the values of some atomic property at the borders of the chart are known, it must be possible to calculate, by two-dimensional iterative averaging, all the values inside the boundary. The boundaries of the most common element charts are orthogonal, so Cartesian coordinates are to be used.

Graphs of r_c and of atomic radius r_ψ (the radius corresponding to the maximum charge density in the outermost orbital, as computed by the Dirac–Breit–Pauli–Hartree–Fock method [17]) globally have positive curvatures along rows and negative curvatures

going down columns. Such graphs lend *qualitative* support to equations (1) or (2) for atomic radii.

The applicability of Laplace's equation can be tested *quantitatively*. At the position of any atom, the sum of the second differences of the data in both the row and the column directions of the periodic charts should be zero.

2.4. The triad principle and Laplace's equation in molecular periodic systems

The manner in which physical periodic systems of molecules are created (section 2.1) guarantees that if atomic descriptors in their chart obey the triad principle, then the same molecular descriptors in their periodic systems will obey it also. For example, consider the species discussed in section 1.2. The triads NaP, MgP, and AlP; MgSi, MgP, and MgS; and BeP, MgP, and CaP are such that the nuclear charge and the total (or valence) electron count of the center molecule can be obtained from the triad principle. This is due to the fact that these descriptors vary linearly, and hence, have zero second differences along the rows and columns; therefore, they satisfy the discretized Laplace equation. The triad MgN, MgP, and MgAs does not behave similarly because of a phenomenon to be discussed in section 2.5. The example applies to molecular weights (subject to isotopic effects); it will be seen below if it applies also to properties such as r_e .

Consider Dias's periodic charts for various polycyclic aromatic hydrocarbons (PAH) [18]. They are "chemical" periodic systems, which means that they include members of a restricted class of molecules (in this case, PAH) without limiting their atom counts. Numerous species descriptors obey the triad principle in these charts. For example, the $C_{20}H_{12}$ lies between $C_{16}H_{10}$ and $C_{24}H_{14}$ in a row, and between $C_{14}H_{10}$ and $C_{26}H_{14}$ in a column, of Dias's table PAH6. The triad principle also works for total electron count and (ignoring isotopic and isomeric effects) molecular weight. These properties vary linearly, have zero second differences along the rows and in the columns, and hence, satisfy the discretized Laplace equation. (Structural properties of PAH such as numbers of isomers, and physical properties such as boiling points (averaged over isomers), do not behave in similar manner.)

Returning to physical periodic systems of diatomic molecules, graphs of r_e are globally smooth (except near alkali-earth pairs) and have one curvature when plotted on C_1 and C_2 (figure 2) and the opposite curvature when plotted on R_1 and R_2 (figure 3) [6]. Thus, since curvatures are related to second differences, the data have second differences of opposite sign along these axes. The *magnitudes* of the second differences are investigated in section 3.3. The plots for other spectroscopic properties (e.g., IP [6]) are less smooth but, on the whole, the curvatures still appear opposite for the two different sets of axes.

The applicability of Laplace's equation to such spectroscopic data must, of course, be tested quantitatively. At the position of any molecule, the sum of the second differences of the data in both the row and the column directions of the periodic charts should be zero. There will certainly be few, if any, sets of molecules such that data for any

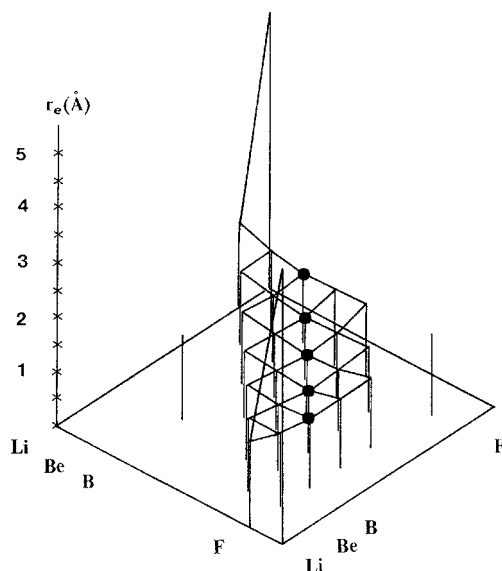


Figure 2. Plot of tabulated r_e of diatomic molecules formed from $(R_1, R_2) = (2, 2)$ atoms. Molecular symbols are formed by using the atomic symbols on the axes; for example, the leftmost datum is B_2 , and the very high data are $NeLi$ and $LiNe$. The valley of minimum values is along the $n_e = 10$ sequence BF , CO , N_2 , OC , and FB (●). The scarcity of data for molecules with fewer than 10 electrons is clearly evident. The curvatures, and hence, the second differences, of the data are positive along both axes. For molecules with other (R_1, R_2) , the plots are very similar, which is the hallmark of diatomic-molecular periodicity. Between two plots with adjacent R_1 or R_2 lie molecules with inert-gas atoms; these molecules have very high values of r_e such as those shown for $NeLi$ and $LiNe$. The regions of these high values are excluded in the testing and use of Laplace's equation presented in this paper. Reproduced by permission from [5].

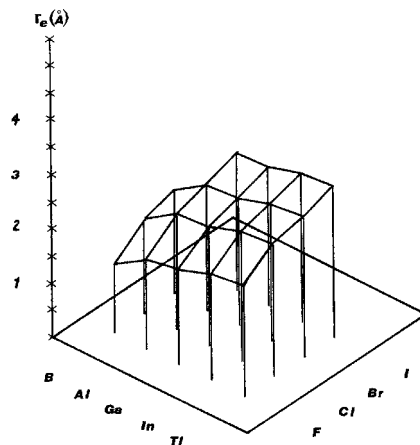


Figure 3. Plot of tabulated r_e formed from group 3 and group 7 atoms. The second differences are negative along both axes, the opposite of the situation in figure 2. Secondary periodicity is clearly visible. Clearly, the edges of such plots are excluded in the testing and use of Laplace's equation. Reproduced by permission from [5].

given spectroscopic property is known for all eight neighbors (figure 1). Thus, it will be necessary to calculate second differences for all existing triads along each direction, average them, and verify that these averages sum to zero.

2.5. Are averaged second-difference sums valid?

It is necessary to inquire about the validity of these proposed averaged second differences. The inquiry must, of course, be empirical, and will consist of comparing them against averages over limited numbers of species. Local failures of smoothness will certainly result in large scatter.

The determination of second differences is complicated by the presence of "secondary periodicity", the phenomenon that atomic numbers and weights, and sometimes properties, increase more abruptly in moving from odd-numbered to even-numbered periods in the last six columns of the chart of the elements, and from even-numbered (beginning with 4) to odd-numbered periods in the first two columns. This increase is due to the first emergences of d and f elements [19,20]. The existence of secondary periodicity suggests the determination of second-nearest-neighbor, rather than nearest-neighbor, second differences in the row direction.

2.6. Can atoms and molecules satisfy Laplace's equation simultaneously?

Rationale has been presented that equation (2) holds for atomic and molecular descriptors such as electron counts, and that it may well hold for r_e and its atomic equivalent, radius. Is it necessarily true that if equation (2) is satisfied by an atomic descriptor or property, then it will also be satisfied by the molecular equivalent?

Consider additive descriptors as a first case, with a numerical example. The atomic numbers and electron populations of Li through Ne are 3 through 10, respectively; the total nuclear charges and the electron populations of LiLi through LiNe and of GaLi through GaNe are 6 through 13 and 34 through 41, respectively. In both cases, the variation in C_2 is linear and any second differences are zero.

More generally, suppose that a property P , with data as exponents in the cells of row R of the chart of the atoms, has a linear variation with respect to C :

$$P = (aC + b)f(R), \quad (3)$$

where a and b are constants. If P is additive (as r_e is, ideally, additive from radii), then its data as exponents in the cells of the periodic system of diatomic molecules will also vary linearly with respect to C_1 and C_2 except for an additive constant. For example, the dependence with respect to C_2 , holding R_1 , R_2 and C_1 constant, is

$$P = (aC_1 + b)f(R_1) + (aC_2 + b)f(R_2) = \text{const}_1 + \text{const}_2 \times (aC_2 + b). \quad (4)$$

The same argument holds if the variation in the atomic property is not linear. For example, suppose that some property of Li through Ne has values $f(R)g(C)$; then the property for LiBe through LiNe has values $f(R_1)g(C_1) + f(R_2)g(C_2)$. For molecules

Table 1
Tabulated atomic covalent radii r_c in Å.

Row	Column of periodic chart						
	1	2	3	4	5	6	7
2	1.519	1.113	0.795	0.772	0.726	0.74	0.709
3	1.858	1.599	1.432	1.176	1.1	1.03	0.994
4	2.272	1.974	1.221	1.225	1.25	1.161	1.142
5	2.48	2.152	1.626	1.405	1.45	1.432	1.333
6	2.655	2.174	1.704	1.75	1.55	1.67	

with various C_1 , the data will vary with C_2 just as for atoms but with an additive constant. The second differences in each case will be the same.

2.7. Can several properties satisfy Laplace's equation simultaneously?

Suppose that, for some property, the average second-nearest-neighbor second differences of the data in the row direction(s) are equal and opposite to the average second differences in the column direction(s). The question then arises, will another property, such as vibration frequency ω_e , with its Walsh's-rule correlation to r_e , also satisfy equation (2)?

It is simple to prove by exception that a function of a solution to Laplace equation will not necessarily satisfy Laplace's equation. Consider the expression $R + C$, clearly a solution of equation (2). Then consider the function $\exp(R + C)$; this function does *not* satisfy equation (2). On the other hand, linear functions of the same expression, such as $\alpha(R + C) + \beta$ (α and β constant), *can* satisfy equation (2).

3. Testing the data as being solutions to the Laplace equation

3.1. Atomic radii

Covalent radii r_c exist for most main-group elements (table 1) [9], and hence, species with known data surround almost all the elements with $2 < R < 6$ and $1 < C < 8$. Tables 2 and 3 show the second differences along the R and C directions. The averages of these second differences, over all elements, have very similar magnitudes and opposite signs (granted that to the confidence of one standard deviation, neither average is statistically significant from zero). The conclusion is that r_c obeys the Laplace equation globally (i.e., with averaging), though with large scatter. The R comparison in table 3 shows the secondary-periodicity effect.

A computed radius, r_ψ , exists; it corresponds to the location of maximum charge density of the outermost orbital [17]. Table 4 shows that the two averages of the nearest-neighbor second differences over all elements for r_ψ have very similar magnitudes and opposite signs (granted that neither average is statistically significant). If second-nearest-neighbors are used, the same is true but now the random errors are less than the magni-

Table 2
Second differences, r_c in Å, along columns.

Row	Column of periodic chart						
	1	2	3	4	5	6	7
2		0.088	0.295	-0.023	0.06	-0.045	
3		0.092	-0.089	0.18	0.006	0.034	
4		-0.455	0.757	0.021	-0.114	0.07	
5		-0.198	0.305	0.266	-0.063	-0.081	
6		0.011	0.516	-0.246	0.32		
Average					0.0711		
Standard deviation					0.2529		

Table 3
Second differences, r_c in Å, down rows.

Row	Column of periodic chart						
	1	2	3	4	5	6	7
3	0.075	-0.111	-0.848	-0.355	-0.224	-0.159	-0.137
4	-0.206	-0.197	0.616	0.131	0.05	0.14	0.043
5	-0.033	-0.156	-0.327	0.165	-0.1	-0.033	
				$R = 3$	$R = 4$	$R = 5$	All rows
Average ($2 < C < 8$)				-0.3446	0.196	-0.0737	-0.074
Standard deviation				0.2939	0.239	0.2029	0.3315

Table 4
Averages of second differences of relativistic Hartree-Fock atomic radii for main-group elements.

	Along rows		Along columns	
	r_ψ in Å	σ	r_ψ in Å	σ
Nearest neighbors	0.073	0.143	-0.079	0.244
Second-nearest neighbors	0.068	0.066	-0.054	0.022

tudes of the averages. The conclusion is that r_ψ obeys the Laplace equation globally, if second differences are used.

3.2. Diatomic-molecular internuclear separations

The r_c data for molecules with atoms from periods groups 1–7 are taken from [10]. There is not one diatomic molecule for which the nearest-neighbor second differences in the data are known for four directions of their chemical space, so it is necessary to compute the averages of the second differences over all the molecules.

Tables 5 and 6 show the molecules for which nearest-neighbor and next-nearest second differences are available. One aspect of these tables is surprising; one might

Table 5
 Nearest-neighbor second differences of main-group diatomic-molecular internuclear separations, r_e in Å, sorted alphabetically.

Molecules, coordinates	Second differences along coordinates							
	R_1	R_2	C_1	C_2				
AlBr	3	4	13	17	0.078	-0.349		
AlCl	3	3	13	17	-0.311	-0.344		-0.003
AlF	3	2	13	17	-0.272		0.042	
AlO	3	2	13	16			0.205	0.023
AlS	3	3	13	16		0.014		
AsO	4	2	15	16		0.054	0.107	0.025
AsP	4	3	15	15	-0.277	0.100		
AsS	4	3	15	16				0.013
BCl	2	3	13	17	-0.280			
BeCl	2	3	2	17				0.141
BO	2	2	13	16				0.137
Br ₂	4	4	17	17	0.043	0.043		
BrAl	4	3	17	13	-0.349	0.078		
BrCl	4	3	17	17	-0.232	0.036		
BrCs	4	6	17	1		0.077		
BrF	4	2	17	17		0.020		
BrGa	4	4	17	13	0.133	0.071		
BrI	4	5	17	17		0.049		
BrIn	4	5	17	13	0.069	-0.116		
BrNa	4	3	17	1	-0.013	0.068		
BrTl	4	6	17	13		0.062		
BS	2	3	13	16				0.058
CaF	4	2	2	17		-0.109		0.012
CaO	4	2	2	16		0.025		
CF	2	2	14	17				0.039
Cl ₂	3	3	17	17	-0.210	-0.210		
ClAl	3	3	17	13	-0.344	-0.311	-0.003	
ClB	3	2	17	13		-0.280		
ClBe	3	2	17	2			0.141	
ClBr	3	4	17	17	0.036	-0.232		
ClCs	3	6	17	1		-0.395		
ClF	3	2	17	17	-0.086	-0.086		
ClGa	3	4	17	13	0.128	-0.277		
ClI	3	5	17	17		-0.263		
ClIn	3	5	13	17	-0.274	-0.116		
CLi	3	2	17	1		-0.307		
ClMg	3	3	17	2		0.093		
CIN	3	2	17	15	-0.131			
ClRb	3	5	17	1	-0.001			
ClTl	3	6	17	13	-0.116	-0.267		
CN	2	2	14	15			0.027	0.035
CO	2	2	14	16			0.187	0.099
CS	2	3	14	16	-0.265			0.033

Table 5
(Continued.)

Molecules, coordinates	Second differences along coordinates							
	R_1	R_2	C_1	C_2	R_1	R_2	C_1	C_2
CsBr	6	4	1	17	0.077			
CsCl	6	3	1	17	-0.395			
FAI	2	3	17	13		-0.272		0.042
FBr	2	4	17	17	0.020			
FC	2	2	17	14			0.039	
FCa	2	4	17	2	-0.109		0.012	
FCl	2	3	17	17	-0.086	-0.086		
FGa	2	4	17	13	0.091		0.163	
FGe	2	4	17	14	0.055		0.020	
FIn	2	5	17	13	-0.112			0.049
FMg	2	3	17	2			0.080	
FRb	2	5	17	1	-0.024			
FSi	2	3	17	14	-0.185		0.024	
FSn	2	5	17	14	-0.085			
FSr	2	5	17	2				0.105
GaBr	4	4	13	17	0.071	0.133		
GaCl	4	3	13	17	-0.277	0.128		
GaF	4	2	13	17		0.091		0.163
GaI	4	5	13	17		0.141		
GeF	4	2	14	17		0.055		0.020
GeO	4	2	14	16		0.093		
GeS	4	3	14	16	-0.265	0.114		
GeSe	4	4	14	16	0.083	0.115		
IBr	5	4	17	17	0.049			
ICl	5	3	17	17	-0.263			
IGa	5	4	17	13	0.141			
IIn	5	5	17	13	-0.119			
IK	5	4	17	1	-0.207			
INa	5	3	17	1	0.017			
InBr	5	4	13	17	-0.116	0.069		
InCl	5	3	17	13	-0.116	-0.274		
InF	5	2	13	17		-0.112	0.049	
InI	5	5	13	17		-0.119		
KI	4	5	1	17		-0.207		
LiCl	2	3	1	17	-0.307			
MgCl	3	3	2	17	0.093			
MgF	3	2	2	17				0.080
N ₂	2	2	15	15			0.127	0.127
NaBr	3	4	1	17	0.068	-0.013		
NaI	3	5	1	17		0.017		
NC	2	2	15	14			0.035	0.027
NCl	2	3	15	17		-0.131		
NO	2	2	15	16			0.113	0.034
NP	2	3	15	15	-0.266		0.083	0.056

Table 5
(Continued.)

Molecules, coordinates	Second differences along coordinates							
	R_1	R_2	C_1	C_2				
NS	2	3	15	16	-0.185			0.028
NSe	2	4	15	16			0.095	0.021
NSi	2	3	15	14			0.135	
OAl	2	3	16	13			0.023	0.205
OAs	2	4	16	15	0.054		0.025	0.107
OB	2	2	16	13			0.137	
OC	2	2	16	14			0.099	0.187
OCa	2	4	16	2	0.025			
OGe	2	4	16	14	0.093			
ON	2	2	16	15			0.034	0.113
OP	2	3	16	15		-0.177		0.083
OS	2	3	16	16	-0.107		0.083	0.132
OSb	2	5	16	15				0.008
OSe	2	4	16	16	0.010			
OSi	2	3	16	14	-0.267		0.074	
OSn	2	5	16	14	-0.119			
OSr	2	5	16	2	-0.078			
OTe	2	5	16	16				0.043
P ₂	3	3	15	15	-0.297	-0.297		
PAs	3	4	15	15	0.100	-0.277		
PbS	6	3	14	16	-0.250			
PbSe	6	4	14	16	0.078			
PN	3	2	15	15		-0.266	0.056	0.083
PO	3	2	15	16	-0.177		0.083	
RbCl	5	3	1	17		-0.001		
RbF	5	2	1	17		-0.024		
S ₂	3	3	16	16	-0.261	-0.261		
SAl	3	3	16	13	0.014			
SAs	3	4	16	15			0.013	
SB	3	2	16	13			0.058	
SbO	5	2	15	16			0.008	
SC	3	2	16	14		-0.265	0.033	
SeGe	4	4	16	14	0.115	0.083		
SeN	4	2	16	15			0.021	0.095
SeO	4	2	16	16		0.010		
SePb	4	6	16	14		0.078		
SeS	4	3	16	16	-0.258	0.047		
SeSi	4	3	16	14	-0.306			
SeSn	4	5	16	14	0.081	-0.114		
SGe	3	4	16	14	0.114	-0.265		
SiF	3	2	14	17		-0.185		0.024
SiN	3	2	14	15				0.135
SiO	3	2	14	16		-0.267		0.074
SiS	3	3	14	16	-0.291	-0.312		

Table 5
(Continued.)

Molecules, coordinates	Second differences along coordinates							
	R_1	R_2	C_1	C_2				
SiSe	3	4	14	16	-0.306			
SN	3	2	16	15	-0.185	0.028		
SnF	5	2	14	17	-0.085			
SnO	5	2	14	16	-0.119			
SnS	5	3	14	16	-0.260	-0.119		
SnSe	5	4	14	16	-0.114	0.081		
SnTe	5	5	14	16		-0.110		
SO	3	2	16	16		-0.107	0.132	0.083
SPb	3	6	16	14		-0.250		
SrF	5	2	2	17			0.105	
SrO	5	2	2	16		-0.078		
SrS	5	3	2	16		-0.056		
SSe	3	4	16	16	0.047	-0.258		
SSi	3	3	16	14	-0.312	-0.291		
SSn	3	5	16	14	-0.119	-0.260		
SSr	3	5	16	2	-0.056			
TeO	5	2	16	16			0.043	
TeSn	5	5	16	14	-0.110			
TlBr	6	4	13	17		0.062		
TlCl	6	3	13	17	-0.267	-0.116		
		Count			79	79	38	38
		Average			-0.100	-0.100	0.072	0.072
		σ			0.154	0.154	0.054	0.054

think that the second differences for a given molecule should be the same in the two row or column directions (and they are so for homonuclear species). But heteronuclear molecules appear twice, with the entries reversed. Some entries that one would expect to see are missing because second differences cannot be found if the molecule is at the end of a row or column (table 5) or at the end and in the compartment once removed from the end (table 6).

The average nearest-neighbor second differences (table 5) have comparable magnitudes and opposite signs in the row and column directions (cf. the end of the table). The averages in the column directions are statistically significant, but those in the row directions have such large scatter that it is impossible to say that they differ from zero. Despite the scatter, it is not excluded that the magnitudes are equal, and hence, that Laplace's equation is, on average, being obeyed. To see if this scatter is due to secondary periodicity, next-nearest-neighbor second differences were found (table 6). Now the results are all statistically significant to a confidence of σ , granted that there are fewer data. The magnitudes are equal and opposite, and hence, Laplace's equation is, on average and to

Table 6
 Second-nearest-neighbor second differences of main-group diatomic-molecular r_e
 in Å, sorted alphabetically by molecules.

Molecules, coordinates	Second differences along coordinates							
	R_1	R_2	C_1	C_2				
AlF	3	3	13	17				0.052
BrGa	4	4	17	13	-0.101			
BrTl	4	6	17	13			0.111	
ClGa	3	4	17	13	-0.102			
FAl	3	3	17	13			0.052	
FGa	2	4	17	13	-0.099		0.090	
FGe	2	4	17	14	-0.081			
FSi	3	3	17	14			0.037	
GaBr	4	4	13	17		-0.101		
GaCl	4	3	13	17		-0.102		
GaF	4	2	13	17		-0.099		0.090
GeF	4	2	14	17		-0.081		
GeO	4	2	14	16		-0.095		0.055
GeS	4	3	14	16		-0.101		0.082
GeSe	4	4	14	16		-0.100		
OGe	2	4	16	14	-0.095		0.055	
OP	2	3	16	15			0.059	
OSi	2	3	16	14				0.053
OSn	3	5	16	14			0.020	
PO	3	2	15	16				0.059
SeGe	4	4	16	14	-0.100			
SGe	3	4	16	14	-0.101		0.082	
SiF	3	3	14	17				0.037
SiO	3	2	14	16			0.053	
SnO	5	3	14	16				0.020
TlBr	6	4	13	17				0.111
TlI	6	5	13	17			0.122	
		Count			7	7	10	10
		Average			-0.097	-0.097	0.068	0.068
		σ			0.008	0.008	0.032	0.032

within the confidence chosen, being obeyed. The scatter cannot be attributed to a slow systematic variation with respect to C_1 and C_2 (figure 4).

3.3. Diatomic-molecular dissociation energies

The data for dissociation potential (D° in eV) were taken from [10]. Only one molecule, Si_2 , has the eight neighbors with data needed for the determination of nearest-neighbor second differences along all four directions R_1 , R_2 , C_1 , and C_2 . The differences along the four directions are 1.3, 1.3, -0.35 , and -0.35 eV, respectively. The discrepancies of 0.95 eV do not preclude the possibility that Laplace's equation is satisfied, be-

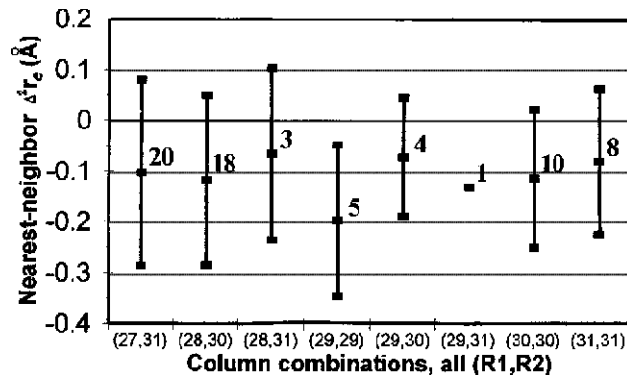


Figure 4. Nearest-neighbor second differences for r_e in Å, plotted on (C_1, C_2) with the numbers indicating the quantity of data, heteronuclear molecules contributing two data each. The error bars designate one σ . No systematic trend is seen.

cause the errors in the data for this property are often as large as 0.16 eV, and because six of them are involved in the error propagation for the difference of two second differences.

A scatter plot of D° against r_e suggests a linear relationship, so according to section 2.7 it is possible that this property also satisfies the Laplace equation, though with much larger σ . Tables 7 and 8 show the second differences. The averaged next-nearest-neighbor data second differences are not different from zero to within the stated confidence; but the magnitudes are equal and opposite, and hence, Laplace's equation possibly, on average, being obeyed. The same appears true for nearest-neighbor second differences, but with less scatter.

4. Mining molecular data with Laplace's equation

4.1. Internuclear separations

The foregoing makes it possible to forecast r_e for individual molecules using the method described in section 1.3. Unfortunately, tabulated data are scarce and the likelihood of having enough neighbors for a target molecule is very small. But fact that the average second differences in both row directions, and in both column directions, are the same indicates that the method should be revisited. Suppose that r_e for NaP, MgP, and AlP are known, and hence, that the second differences with respect to the group number of their first atoms is known. Then the second difference of r_e with respect to the group number of the second atoms will be the same. So, if r_e is known for MgSi, then the hypothetically unknown value for MgS can be estimated from the second difference of the triad MgSi, MgP, and MgS. Thus, it is quite possible that r_e can be found for some target molecule.

The likelihood of making *global* forecasts for r_e remains low because having molecules with known data completely surrounding an ensemble of target molecules is most improbable.

Table 7
 Nearest-neighbor second differences of main-group diatomic dissociation potentials in eV, sorted alphabetically by molecules.

	Molecules, coordinates				Second differences along coordinates			
	R_1	R_2	C_1	C_2	R_1	R_2	C_1	C_2
AlBr	3	4	13	17	-0.07	0.03		
AlCl	3	3	13	17	0.18	1.08		
AlF	3	2	13	17	0.01			-3.46
AlO	3	2	13	16	1.65			
AlP	3	3	13	15	1.54		1.78	
AlS	3	3	13	16		0.99	-0.36	
AlSe	3	4	13	16		-0.23		
AlSi	3	3	13	14			-0.93	
BaBr	6	4	2	17		1.39		0.01
BaCl	6	3	2	17		0.74		-0.7
BaF	6	2	2	17				-2.38
BaI	6	5	2	17				-2.52
BCl	2	3	13	17		1.3		
BeO	2	2	2	16				2.57
BiS	6	3	15	16		-0.07		
BiSe	6	4	15	16		-0.03		
BO	2	2	13	16				-0.87
BP	2	3	13	15			1.84	
BrAl	4	3	17	13	0.03	-0.07		
BrBa	4	6	17	2	1.39		0.01	
Br ₂	4	4	17	17	0.11	0.11		
BrCa	4	4	17	2			1.65	
BrCl	4	3	17	17	0.17	0.06		
BrCs	4	6	17	1	-0.2			
BrF	4	2	17	17	0.39			
BrGa	4	4	17	13	-0.21	-0.18		
BrI	4	5	17	17	0.05			
BrIn	4	5	17	13	-0.11	-0.26		
BrK	4	4	17	1	-0.17	-0.18		
BrLi	4	2	17	1	-0.28			
BrNa	4	3	17	1	-0.25	0.76		
BrO	4	2	17	16	-0.25		0.65	
BrRb	4	5	17	1	-0.2	0.28		
BrSr	4	5	17	2		0.25	1.07	
BrTl	4	6	17	13	-0.26		-0.5	
BS	2	3	13	16		1.01	-2.96	-0.86
CaBr	4	4	2	17				1.65
CaCl	4	3	2	17	-0.73	0.58		1.08
CaF	4	2	2	17	-0.63			0.09
C ₂	2	2	14	14			-0.06	-0.06
CF	2	2	14	17				-0.03
ClAl	3	3	17	13	1.08	0.18		
ClB	3	2	17	13	1.3			

Table 7
(Continued.)

Molecules, coordinates	Second differences along coordinates								
	R_1	R_2	C_1	C_2					
ClBa	3	6	17	2	0.74		-0.7		
ClBr	3	4	17	17	0.06	0.17			
ClCa	3	4	17	2	0.58	-0.73	1.08		
Cl ₂	3	3	17	17	-0.11	-0.11			
ClCs	3	6	17	1	0.16				
ClF	3	2	17	17	-1.09				
ClGa	3	4	17	13	0.44	-0.28			
ClI	3	5	17	17	0.39				
ClIn	3	5	17	13	0.36	-0.14			
ClK	3	4	17	1	0.3	-0.15			
CLi	3	2	17	1	0.56				
ClMg	3	3	17	2			2.77		
ClNa	3	3	17	1	-1.97	0.72			
ClO	3	2	17	16	-0.87				
ClRb	3	5	17	1	0.3	0.32			
ClSr	3	5	17	2	0.67	0.32	0.42		
ClTl	3	6	17	13	0.35				
CN	2	2	14	15			1.78		
CO	2	2	14	16			-8.75	-7.4	
CP	2	3	14	15			1.44	-0.64	
CS	2	3	14	16		2.35			-3.91
CsBr	6	4	1	17	-0.2				
CsCl	6	3	1	17	0.16				
CSi	2	3	14	14	1.66				
FAI	2	3	17	13	0.01	-3.46			
FBa	2	6	17	2			-2.38		
FBr	2	4	17	17		0.39			
FC	2	2	17	14			-0.03		
FCa	2	4	17	2	-0.63	0.09			
FCl	2	3	17	17	-1.09				
FGa	2	4	17	13	0.18	-1.48			
FGe	2	4	17	14	0.47	0.18			
FIn	2	5	17	13	0.05	-0.02			
FN	2	2	17	15			0.9		
FO	2	2	17	16			0.64		
FRb	2	5	17	1		0.22			
FSi	2	3	17	14	-0.47				
FSn	2	5	17	14	-1.2				
FSr	2	5	17	2		0.37	-0.91		
FTl	2	6	17	13			0.51		
GaBr	4	4	13	17	-0.18	-0.21			
GaCl	4	3	13	17	-0.28	0.44			
GaF	4	2	13	17	0.18				-1.48
GaI	4	5	13	17	0.26				

Table 7
(Continued.)

	Molecules, coordinates				Second differences along coordinates			
	R_1	R_2	C_1	C_2	R_1	R_2	C_1	C_2
GaTe	4	5	13	16	-0.54			
GeF	4	2	14	17	0.47			0.18
GeO	4	2	14	16	0.19			
GeS	4	3	14	16	-0.15	0.42		
GeSe	4	4	14	16	-0.12	-0.05		
GeSi	4	3	14	14		1.39		
GeTe	4	5	14	16	-0.15			
IBa	5	6	17	2			-2.52	
IBr	5	4	17	17		0.05		
ICl	5	3	17	17		0.39		
IGa	5	4	17	13		0.26		
I ₂	5	5	17	17	-0.87	-0.87		
IIn	5	5	17	13		-0.63		
IK	5	4	17	1		-0.32		
INa	5	3	17	1		0.85		
InBr	5	4	13	17	-0.26	-0.11		
InCl	5	3	13	17	-0.14	0.36		
InF	5	2	13	17	0.05			-0.02
InI	5	5	13	17	-0.63			
InS	5	3	13	16				2.45
InSe	5	4	13	16		0.09		
InTe	5	5	13	16			0.59	
IRb	5	5	17	1		0.27		
KBr	4	4	1	17	-0.18	-0.17		
KCl	4	3	1	17	-0.15	0.3		
KI	4	5	1	17	-0.32			
LiBr	2	4	1	17		-0.28		
LiCl	2	3	1	17		0.56		
MgCl	3	3	2	17				2.77
NaBr	3	4	1	17	0.76	-0.25		
NaCl	3	3	1	17	0.72	-1.97		
NaI	3	5	1	17	0.85			
Na ₂	3	3	1	1	0.23	0.23		
NC	2	2	15	14				1.78
NF	2	2	15	17				0.9
N ₂	2	2	15	15			-5.26	-5.26
NO	2	2	15	16			0.26	3.21
NP	2	3	15	15				-1.29
NS	2	3	15	16				3.12
OAl	2	3	16	13		1.65		
OB	2	2	16	13			-0.87	
OBe	2	2	16	2			2.57	
OB _r	2	4	16	17	-0.25			0.65
OC	2	2	16	14			-7.4	-8.75

Table 7
(Continued.)

Molecules, coordinates	Second differences along coordinates							
	R_1	R_2	C_1	C_2				
OCl	2	3	16	17	-0.87			
OF	2	2	16	17				0.64
OGe	2	4	16	14	0.19			
ON	2	2	16	15			3.21	0.26
O ₂	2	2	16	16			-1.51	-1.51
OP	2	3	16	15			1.32	
OS	2	3	16	16			-1.82	
OSi	2	3	16	14	1.35		-5.1	
OSn	2	5	16	14	-0.37			
PAI	3	3	15	13	1.54			1.78
PB	3	2	15	13				1.84
PbS	6	3	14	16	-0.07			
PbSe	6	4	14	16	-0.12			-1.34
PbTe	6	5	14	16				0.72
PC	3	2	15	14			-0.64	1.44
PN	3	2	15	15			-1.29	
PO	3	2	15	16				1.32
P ₂	3	3	15	15			-1.79	-1.79
PS	3	3	15	16	0.8			1.71
PSe	3	4	15	16	0.08			
PSi	3	3	15	14			-0.23	2.17
RbBr	5	4	1	17	0.28	-0.2		
RbCl	5	3	1	17	0.32	0.3		
RbF	5	2	1	17	0.22			
RbI	5	5	1	17	0.27			
SAl	3	3	16	13	0.99			-0.36
SB	3	2	16	13	1.01		-0.86	-2.96
SBi	3	6	16	15	-0.07			
SbTe	5	5	15	16				0.77
SC	3	2	16	14	2.35		-3.91	
SeAl	4	3	16	13	-0.23			
SeBi	4	6	16	15	-0.03			
SeGe	4	4	16	14	-0.05	-0.12		
SeIn	4	5	16	13	0.09			
SeP	4	3	16	15	0.08			
SePb	4	6	16	14	-0.12		-1.34	
SeSi	4	3	16	14	-0.22	-0.32	-4.15	
SeSn	4	5	16	14	0.06	-0.34		
SGe	3	4	16	14	0.42	-0.15		
SiAl	3	3	14	13				-0.93
SiC	3	2	14	14	1.66			
SiF	3	2	14	17	-0.47			
SiGe	3	4	14	14	1.39			
SIn	3	5	16	13			2.45	

Table 7
(Continued.)

	Molecules, coordinates				Second differences along coordinates			
	R_1	R_2	C_1	C_2	R_1	R_2	C_1	C_2
SiO	3	2	14	16	1.35			-5.1
SiP	3	3	14	15			2.17	-0.23
SiS	3	3	14	16	0.19	1.06		-4.46
SiSe	3	4	14	16	-0.32	-0.22		-4.15
Si ₂	3	3	14	14	1.3	1.3	-0.35	-0.35
SiTe	3	5	14	16				-3.55
SN	3	2	16	15			3.12	
SnF	5	2	14	17	-1.2			
SnO	5	2	14	16	-0.37			
SnS	5	3	14	16	-0.38	0.15		
SnSe	5	4	14	16	-0.34	0.06		
SnTe	5	5	14	16	-0.59			-2.39
SO	3	2	16	16				-1.82
SP	3	3	16	15	0.8		1.71	
SPb	3	6	16	14	-0.07			
SrBr	5	4	2	17	0.25			1.07
SrCl	5	3	2	17	0.32	0.67		0.42
SrF	5	2	2	17	0.37			-0.91
SrS	5	3	2	16	0.86			
SSi	3	3	16	14	1.06	0.19	-4.46	
SSn	3	5	16	14	0.15	-0.38		
SSr	3	5	16	2		0.86		
TeGa	5	4	16	13		-0.54		
TeGe	5	4	16	14		-0.15		
TeIn	5	5	16	13				0.59
TePb	5	6	16	14			0.72	
TeSb	5	5	16	15			0.77	
TeSi	5	3	16	14			-3.55	
TeSn	5	5	16	14		-0.59	-2.39	
TlBr	6	4	13	17		-0.26		-0.5
TlCl	6	3	13	17		0.35		
TlF	6	2	13	17				0.51
		Count			99	99	60	60
		Average			0.166465	0.166465	-0.60033	-0.55117
		σ			0.661182	0.661182	2.457001	2.503583

4.2. Dissociation energies

The difficulty just described is removed for diatomic D_0° . All four sides of the mesh containing molecules with a given R_1 and R_2 have known data (figure 5): if C_1 or C_2 are 0 or 8 (18 in the IUPAC scheme) then the molecules contain an inert-gas atom and D_0° is essentially zero. These boundary conditions would, of course, produce the trivial

Table 8
 Second-nearest-neighbor second differences of dissociation potential in eV,
 sorted alphabetically by molecules.

Molecules, coordinates	Second differences along coordinates							
	R_1	R_2	C_1	C_2	R_1	R_2	C_1	C_2
AlO	3	2	16	13				-0.448
AlP	3	3	15	13			0.5675	
AsF	4	2	17	15				0.0325
AsGa	4	4	13	15				0.335
BBr	2	4	17	13				-0.438
BF	2	2	17	13				-1.553
BO	2	2	16	13				-1.643
BrB	4	2	13	17			-0.438	
BrGa	4	4	13	17		-0.173		
BrK	4	4	1	17		0.17		
BrN	4	2	15	17			0.31	
CaS	4	3	16	2	0.31			
ClGa	3	4	13	17		-0.13		
ClK	3	4	1	17		0.185		
ClTl	3	6	13	17			0.005	
CN	2	2	15	14			-1.313	
CO	2	2	16	14				-3.115
CS	2	3	16	14				-1.39
FAs	2	4	15	17			0.0325	
FB	2	2	13	17			-1.553	
FGa	2	4	13	17		0.105	-0.673	
FGe	2	4	14	17		-0.183		
FK	2	4	1	17		0.23		
FN	2	2	15	17				0.6025
GaAs	4	4	15	13				0.335
GaBr	4	4	17	13	-0.173			
GaCl	4	3	17	13	-0.13			
GaF	4	2	17	13	0.105			-0.673
GeF	4	2	17	14	-0.183			
GeO	4	2	16	14	0.34			
GeS	4	3	16	14	-0.123			
GeSe	4	4	16	14	-0.225			
IK	5	4	1	17		0.12		
InSb	5	5	15	13			0.34	
KBr	4	4	17	1	0.17			
KCl	4	3	17	1	0.185			
KF	4	2	17	1	0.23			
KI	4	5	17	1	0.12			
NBr	2	4	17	15				0.31
NC	2	2	14	15				-1.313
NF	2	2	17	15				0.6025
NO	2	2	16	15				-0.623

Table 8
(Continued.)

Molecules, coordinates	Second differences along coordinates							
	R_1	R_2	C_1	C_2	R_1	R_2	C_1	C_2
OAl	2	3	13	16			-0.448	
OB	2	2	13	16			-1.643	
OC	2	2	14	16			-3.115	
OGe	2	4	14	16		0.34		
ON	2	2	15	16			-0.623	
OP	2	3	15	16			-1.07	
PAI	3	3	13	15				0.5675
PO	3	2	16	15				-1.07
SbIn	5	5	13	15				0.34
SC	3	2	14	16			-1.39	
SCa	3	4	2	16		0.31		
SeGe	4	4	14	16		-0.225		
SGe	3	4	14	16		-0.123		
TICl	6	3	17	13				0.005
Count					12	12	17	17
Average					0.052	0.052	-0.592	-0.592
σ					0.206	0.206	0.996	0.996

0	0	0	0	0	0	0	0	0	0	He
0									0	Li
0									0	Be
0								7.81	0	B
0						11.09	5.71	0	0	C
0					9.76	7.44	3.92	0	0	N
0					6.5	5.12	2.23	0	0	O
0				11.1	7.44	5.00	2.55	0	0	F
0				7.81	5.71	3.92	2.55	1.27	0	F
0				5.67	3.5	2.23	1.6	0	0	Ne
0	0	0	0	0	0	0	0	0	0	Ne
He	Li	Be	B	C	N	O	F	Ne		

Figure 5. Row-2 diatomic molecules are plotted in the space C_1, C_2 . Dissociation potentials (in eV) are shown for molecules containing inert-gas atoms, for those on $n_e = 10$, and for those in the triangular region at the lower right. Inside that region, values obtained by iterative interpolation are shown in italic.

result everywhere in the mesh, so a high-value boundary must be found. This high-value boundary is the line along which lie molecules with 10 valence electrons ($n_e = 10$); the data for molecules on it are known (for $R_1 = R_2 = 2$ as seen in figure 5); and that the cohort of molecules on it and going in the directions of increasing group numbers to C_1 or $C_2 = 7$ are those of more interest in much of chemistry.

The results of iterative interpolation for these molecules are seen in the figure. Nearest-neighbor triads were used, because only one prediction (O_2) would be possible with second-nearest-neighbor triads. The average difference between the tabulated values and the interpolated data is 1.4% ($\sigma = 14.7\%$) [21]. This result is much better than any achieved by the selection of graphically-based starting equations for least-squares analysis.

The predictions just described utilize only two of the four dimensions of the periodic system of diatomic molecules. What about an iterative averaging along all four coordinates? The process has been carried out in four dimensions to find D_o° for main-group molecules within the same triangular area shown in figure 4 but having both atoms from row 3 (Na to Cl) [22]. Nearest-neighbor triads were used. Utilizing 101 tabulated values and, where tabulated data were lacking, 25 neural-network forecasts [8], it was possible to predict six values for D_o° of $R_1 = R_2 = 3$ molecules (SiCl, PS, PCl, S_2 , SCl, and Cl_2). The average of the differences between the predictions and tabulated values (where they exist, i.e., for PS, Cl_2 and S_2) is -8.35% ($\sigma = 14.8\%$). The accuracy is not as good as for the two-dimensional case, but serves to illustrate the method.

5. Discussion

It is concluded that r_e satisfies the Laplace equation sufficiently well to make reasonably good individual predictions when there are sufficient neighboring molecules with tabulated data. D_o° obeys Laplace's equation but with larger random errors; in spite of these errors, the results of iterative interpolation are useful for first-approximation forecasts. The triad principle (in the form of Laplace's equation), thus, rejoins the indices of mathematical chemistry, the correlations of QSPR, and least-squares and neural network analyses as tools for mining molecular data while results from precise experiment and computation are awaited.

Computer experiments done in the course of this work demonstrated that Poisson's equation (formed by adding to the second differences a term with the central molecule's datum multiplied by a constant c) do not smooth the data well. This equation would have been equivalent to Schrödinger's time-independent equation (with the constant c being $2mV/\hbar^2$ and V being a constant "chemical-space potential"). Additional experiments with V as a *variable* showed that it fluctuates with short wavelength and with no physical meaning. How ironic it would have been if either of these computer experiments had succeeded!

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