Discrete vector calculus on periodic systems of atoms and molecules

Ray Hefferlin

Physics Department, Southern Adventist University, Collegedale, TN 37315, USA
E-mail: hefferln@southern.edu

In this paper we combine atomic and molecular data, which are displayed in their periodic systems, in such a way as to take the discrete gradient. Then we act on the resulting vector field with the discrete vector divergence. The curl is obviously zero; the scalar field is conservative. We act on the original data with the discrete Laplacian operator (the iterated average utilizing only data on a border which contains the extreme values). The properties considered are atomic electronegativity, ionization potential and radius; and diatomic-molecular dissociation potential and internuclear separation. The calculus should work well to highlight the local energy minima of the nuclear valley of stability.

KEY WORDS: vector operators, element chart, molecular chart, periodicity

1.   Introduction

Consider the values of some property archived at the locations of the elements on a flat, orthogonal, and preferably compact, periodic table or at the locations of diatomic molecules on a cross-section of their periodic system. Data for alloys lying between the locations of atomic elements, and for Bertheloid species lying between molecules, will be ignored. We characterize the values as vector fields by taking what amounts to a discrete gradient; this allows for visualization that complements the use of contours. The divergence of the vector field can highlight features such as secondary periodicity. We take the iterative average of the data by forming what amounts to the discrete Laplacian and this allows for the prediction of data.

1.1.   Theory

Any property is designated as P and its values for the atomic elements are denoted as $P(x, y) \equiv P(C, R)$, where C is the group number and R is the period number. A unit cell of the field has corners ul (upper left), ur, ll, and
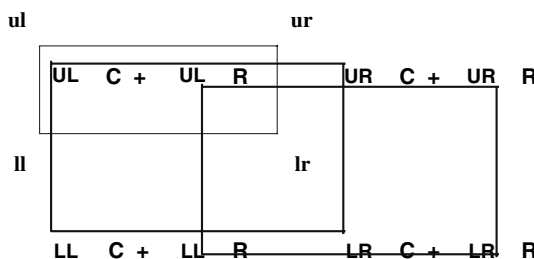
Figure 1. A portion of the discrete space. The corners of a unit cell (four atoms) are designated with lower-case letters. The data there determine the two components of the vector (smaller box) at the center of the cell according to Eq. (1). Four such vectors are indicated, each with unit vectors **C** and **R**. Their "amplitudes," such as **UL**, indicate the positions of these vectors with respect to each other. The four **R** amplitudes, and the four **C** amplitudes, (at the vertices of the larger boxes) are combined to determine the divergence at the center of the *figure*, **lr**, according to Eq. (2). This position coincides with that of an element in the periodic chart.

lr (lower right). The discrete operators defined here are used in many texts on mechanics and electrodynamics in the process of deriving the theorems of Gauss and Stokes, especially older ones (For instance [1, 2]).

The gradient is

$$\mathbf{V} = \nabla P = \{[(ur - ul) + (lr - ll)]/2\}\mathbf{C} + \{[(ur - lr) + (ul - ll)]/2\}\mathbf{R} \qquad (1)$$

where **C** and **R** are unit vectors in the directions of increasing group and period number in the chart of the elements. All four sides of the cell (figure 1) are used in the definition of the vector, which is therefore defined as at the *center* of the cell. This vector differs from those often seen on charts of the nucleids: it is not at the location of, and does not represent, an individual object and it does not represent a transmutation. The components will be negative if the average horizontal or vertical values decrease to the left or downward.

The divergence is found from the vectors **V** at the centers of four adjacent cells, as shown in figure 1.

$$\begin{aligned} \nabla \cdot \mathbf{V} &= \{[(UR - LR) + (UL - LL)]/2\} \cdot 1 \\ &\quad + \{[(UR - UL) + (LR - UR)]/2\} \cdot 1 \end{aligned} \qquad (2)$$

The first term is the change in the averaged left and right *vertical* components of the vector field, $\mathbf{V}_R$, flowing through the unit-length *horizontal* sides of the *rectangle* shown in figure 1. The capital letters differ in meaning from the lower-case letters used above; they indicate which vertical component of four vectors, $\mathbf{V}_R$, is being used. The second term is the change in the averaged upper and lower horizontal components of the vector, $\mathbf{V}_C$, flowing through the unit-length vertical sides of the second rectangle imagined in the figure. The divergence thus defined exists at the element locations in the centers of the *cells*, lacking those
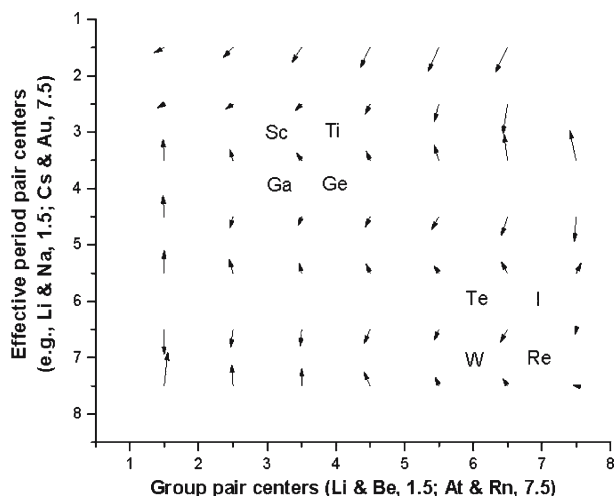
Figure 2. The vector field of *en* for the elements in short form of the periodic table (ignoring the rare-earth elements). Vector magnitudes are relative; a few element positions are shown to illustrate how four of them are needed to define one vector.
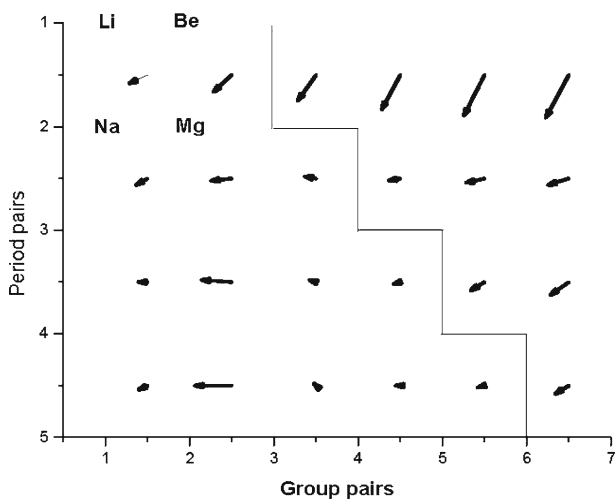

Figure 3. Same as figure 2 except for the short main-group portion of the periodic table. the line of metalloids is shown.

at the edges (which are sacrificed to define the vectors). The chemical element is a source if the net flow out of the four sides of the unit cell is positive.

The Laplacian $\nabla^2 P$ is found for elements at locations (C, R) in the periodic table by *iterative* averaging, in the C and R directions, using only the known values (which must include the extreme values) on a boundary of the region [3].

Li	Be	B	C	N	O	F
	1.5	2.0	2.5	3.0	3.5	
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
	1.4	*1.8*	*2.3*	*2.6*	*2.9*	
K	Ca	Ga	Ge	As	Se	Br
0.8	1.0	1.6	1.8	2.0	2.4	2.8
	1.3	*1.7*	*2.0*	*2.3*	*2.6*	
Rb	Sr	In	Sn	Sb	Te	I
0.8	1.0	1.7	1.8	1.9	2.1	2.5
	1.1	*1.6*	*1.9*	*2.1*	*2.3*	
Cs	Ba	Tl	Pb	Bi	Po	At
	0.9	1.8	1.8	1.9	2.0	

Figure 4. The values of $\nabla^2(en)$, the iterated averages, of *en* for the elements in the space with corners at Mg, S, Sr, and Te are shown in italics. The tabulated values are shown in normal font; those at the four outer corners are not needed.

Now consider the values of some property archived at the locations of diatomic molecules in their four-dimensional periodic system [4, 5]. The definitions given above can be applied immediately to molecules lying in a plane section of the periodic system, such as one defined by fixed atomic period numbers R_1 and R_2.

2. Results

2.1. Electronegativity

Figure 2 shows **V** for Pauling electronegativities [6] (*en*) on the "short form" of the element chart (omitting H, He, Ne, and Ar). The vectors are located at half-integer coordinates. The periods are arbitrarily defined with Li, Na, K, Cu, Rb, Ag, Cs, and Au starting periods 1–8; the elements in group 8 are Fe, Kr,
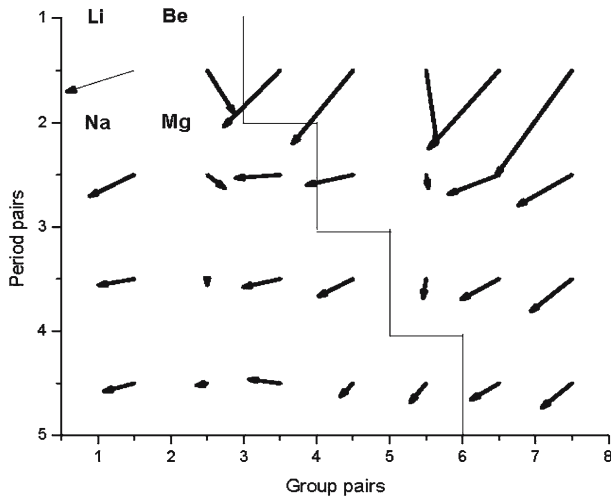
Figure 5. The same as figure 3 except for *IP*, along with the line of metalloids. The four atoms shown define the thin vector at top left.
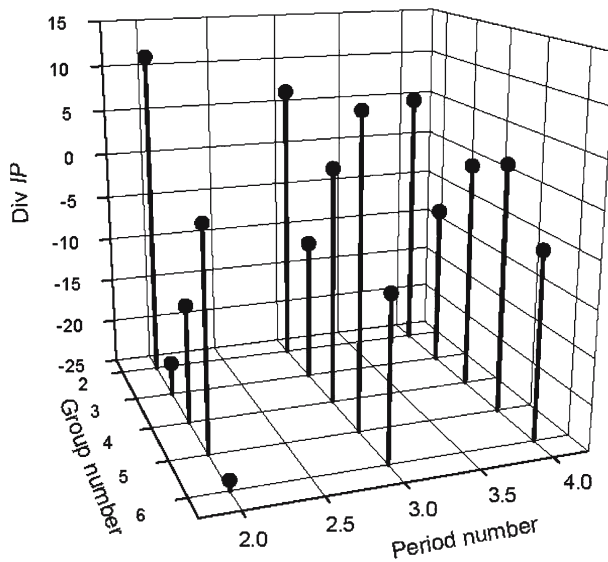

Figure 6. Divergences derived for the vectors in figure 5.

Ru, Xe, Os, and Rn. The rare-gas *en* are given in [7]. The alternating vector directions show a defect of this chemical form of the periodic chart. Figure 3, includes only the main-group elements, with Li, Na, K, Rb, and Cs starting periods 1 through 5; it has only a very small alternation.

Figure 4 shows $\nabla^2(en)$ in the main-group portion of the periodic chart. Only the tabulated values on the border of the rectangle were used to compute
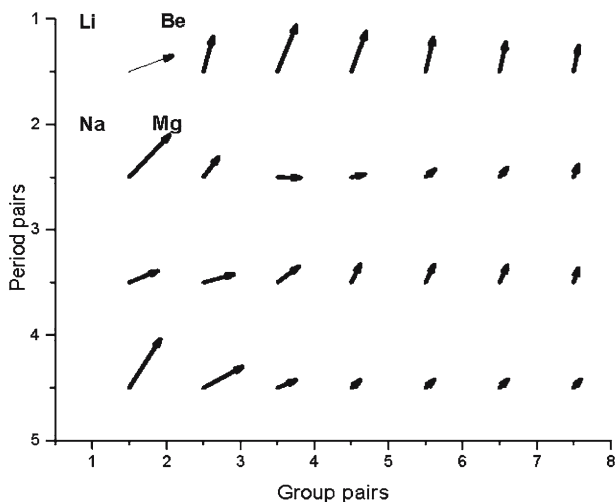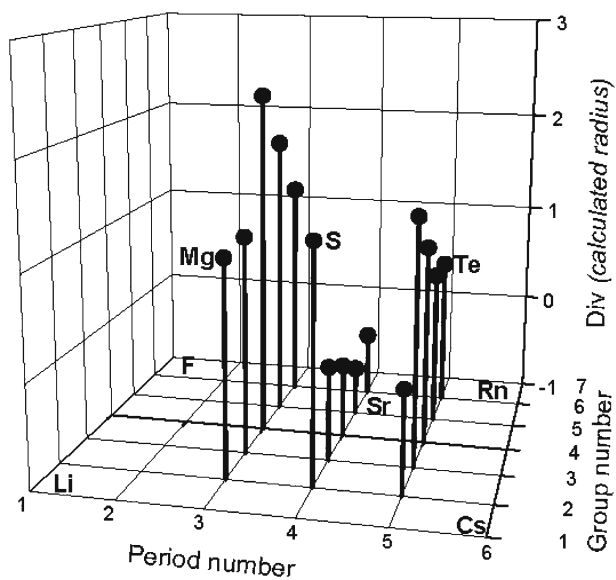
Figure 7. Same as figure 3 for r_P.

Figure 8. Divergences derived for the vectors in figure 7. The named atomic locations are at the corners of the array; the highest value pertains to silicon.

the Laplacian. The averages of the absolute percentage differences of the Laplacians from the tabulated values is 14% with $\sigma = 7.4\%$, adequate for rough estimation.
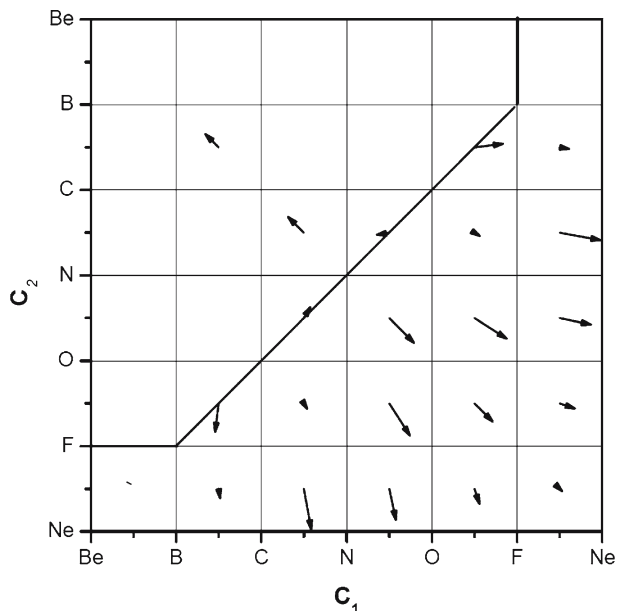
Figure 9. The vector field of D_o^o for the diatomic molecules formed from row-2 atoms. The diagonal line with horizontal and vertical termina represents the path of least descent from the maximum value(s) at CO and OC to the low value at BeF and FBe [14]. N_2 has a slightly lower D_o^o than the maximum values, so the directions of the short vectors are almost parallel to the diagonal line. Vector magnitudes are relative.

2.2. Ionization potential

Figure 5 gives the gradients for ionization potentials (*IP*) [8]. The much larger vector magnitudes in the top row are a result of the "edge effect," i.e., the relatively much higher (or for some properties lower) values in the period containing Li to Ne. The divergences of the field are presented in figure 6. The periodicity as the group numbers change in the periods (numbered as above) is obvious. The Laplacian results for *IP* have been presented previously [9].

2.3. Atomic radii

The gradients for r_ψ (the radii of maximum charge density in the outermost orbital antinodes) [10] are in figure 7 and the divergences are in figure 8. The alternation of amplitudes in figure 7 and the consequent valley in figure 8 are clear manifestations of second periodicity [11]. $\nabla^2(r_\psi)$ has been discussed earlier [12]. The gradients for r_{cov} (the covalent radius) [13], not shown, are, not surprisingly, similar to those in figure 7. Also not shown are $\nabla^2(r_{cov})$, for which the
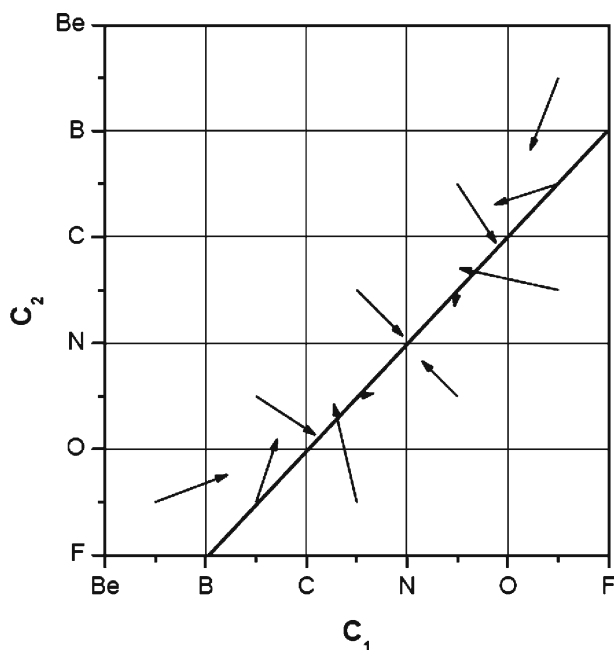
Figure 10. The vector field of r_e for the diatomic molecules formed from available data for molecules containing row-2 atoms.

average of the absolute percent differences from the tabulated values is 7.7% with $\sigma = 6.6\%$.

2.4. Molecular dissociation potential

Data for properties of fixed-period diatomic molecules, plotted on the atomic group-number coordinates C_1 and C_2, lie in an orthogonal lattice just as do data for atoms in the element chart, although unfortunately many of their values are unknown. Results for **V** of dissociation potentials $(D_o{}^o)$ [14] are presented in figure 9. That so many vectors are defined in the figure is due to the fact that this property has essentially zero-magnitude values for rare-gas molecules.

It can be expected from figure 9 that the divergences at N_2, NO, and CF are larger and those at O_2, F_2, OF, and NF are smaller. The Laplacian field $\nabla^2(D_o{}^o)$ has been presented earlier [12, 15, 16]. The iterative averaging procedure predicts the values for five non-redundant molecules (CF, OF, F_2, NO, and O_2); the average of the absolute differences from the tabulated values is 1.42% (with $\Phi = 14.7\%$, which shows that discrepancies for individual molecules are fairly large). A preliminary discussion of how to visualize this procedure in four (non-orthogonal) dimensions is given in [16].

2.5. Molecular internuclear separation

The gradients for the internuclear separation (r_e) [14] are shown in figure 10. Their general tendency is opposite to that of D_o^o except that the minimum is at N_2 and not at CO and OC. For both properties, the results for higher-period molecules must be similar to those with $(R_1, R_2) = (2, 2)$ [17, 18] except that in cases like $(R_1, R_2) = (2, 3)$ the display is no longer symmetrical with respect to reflection through the line from upper left to lower right. Also, for higher-period molecules there are fewer and fewer data. From the vectors in figure 10 one can derive only two values of the divergence.

References

[1] J.C. Slater and N.H. Frank, *Mechanics* (McGraw-Hill, New York, 1947).

[2] G.P. Harnwell, *Principles of Electricity and Electromagnetism, McGraw-Hill* (New York, 1949).

[3] H.D. Young and R.A. Freedman, *University Physics* (Addison Wesley Longman, San Francisco, 2000).

[4] R.A. Hefferlin, G.V. Zhuvikin, K.E. Caviness and P.J. Duerksen, J. Quant. Sperctrosc. Radiat. Transfer 32 (1984) 257.

[5] R. Hefferlin, J. Chem. Inf. Comput. Sci. 34 (1994) 314.

[6] Periodic Table of the elements (chart), Sargent-Welch, New York, 1969.

[7] http://www.lenntech.com/Periodic-chart-elements/electronegativity.htm

[8] Handbook of Chemistry and Physics, Vol. 54 (Chemical Rubber Corporation Publishers, 1964).

[9] R.A. Hefferlin, Field Theory for Chemical Spaces, *AMS/IP Studies in Advanced Mathematics*, Vol. 13, 1999.

[10] S. Fraga and J. Karwowski, *Handbook of Atomic Data* (Elsevier Scientific, Amsterdam, 1976).

[11] V.A. Latysheva and R. Hefferlin, J. Chem. Inf. Comput. Sci. 44 (2004) 1202.

[12] R. Hefferlin, Numerical Solutions of the Laplace Equation in Chemical Spaces, *DIMACS Series in Discrete Mathematics and Theoretical Computer Sciences*, Vol. 51, 2000 (the caption of figure 1 is wrong and the section headings should refer to "Atoms").

[13] J.A. Campbell, *Chemical Systems* (Freeman, San Francisco, 1970).

[14] K.P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reihold, New York, 1979).

[15] R. Hefferlin, J. Mol. Structure (Theochem) 506 (2000) 71.

[16] R. Hefferlin and J. Knoll, J. Math. Chem. 28 (2000) 169.

[17] R. Hefferlin and M. Kutzner, J. Chem. Phys. 75 (1981) 1035.

[18] R. Hefferlin, *Periodic Systems of Molecules and their Relation to the Systematic Analysis of Molecular Data* (Edwin Mellen Press, Lewiston, New York, 1989).