

INTERPOLATION FORMULAE FOR DESCRIBING SIZE DEPENDENCE OF PROPERTIES OF FINITE SYSTEMS AND THEIR USE FOR CLUSTERS AND BIOLOGICALLY IMPORTANT MOLECULES*

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ABSTRACT

The general possibility of introducing simple interpolation formulae for the size dependence of the properties of finite systems together with examples of their use for clusters and biologically important macromolecules is discussed.

INTRODUCTION

There are numerous examples showing that the size dependence of the physical properties of atomic clusters, macromolecules and other finite systems can be successfully described by remarkably simple formulae in which only the dependence on the size of the system (or the number of atoms N) is considered. We discuss first the cluster properties; the shape of the cluster or the concrete form of the surface boundary conditions do of course play an important role in determining the size dependence of the cluster properties. It appears, however, at least for larger clusters, that the number of atoms N is of primary importance and the surface boundary conditions play only a secondary role. An approximate formula describing the size dependence of the measured quantity Q has, in general, the form of the Taylor expansion.

$$Q(N) = Q(\infty) (1 + c_1/N^{1/d} + c_2/N^{2/d} + \dots) \quad (1)$$

in the variable $1/N^{1/d}$. Here, $Q(\infty)$ is the value of the quantity for the infinite system ($N \rightarrow \infty$), c_1 and c_2 are constants depending on the considered quantity, the properties of the atoms forming the cluster, the structure of the cluster and other conditions. The number $d = 1, 2$ or 3 denotes the number of dimensions

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in which the system grows. For a cluster, d is equal to 3. For a thin film with N atomic layers d equals 1.

The interpolation formulae of the form of eqn. (1) have been successfully applied to different electron, geometric and thermodynamic properties of various clusters and thin films. The quantities which have been interpolated in this way are the electron binding energy [1-15], the band width [2,4-5], the lowest occupied molecular orbital (MO) [2,4-5], the ionization potential and work function [13,16-20], the lattice constant [1], the distance of the CO molecule from the surface of the solid [1], the entropy [1], the free energy [1], the position of the Mie resonant absorption [1], the specific resistance of thin films [1], the contact potential [21], the surface stress and tension [22] and other properties [1,23-27]. The first example we give here is the formula for the ionization potential (IP, in eV) of Na clusters.

$$IP^{Na}(N) = (2.75 + 2.389/N^{1/3}) \quad (2)$$

Starting from $N=5$, eqn. (2) gives a reasonable description of the experimental data with an error of less than 0.2 eV. The second example is the formula for the size-dependent part of the entropy of Al particles as a function of their radius R (in Å) [1]

$$\Delta S^{Al}(R)/k = 7.8/R \quad (3)$$

where k is Boltzmann's constant. This formula is in good agreement with experimental data starting from $R \approx 15$ Å.

Note that for $d=3$ and the spherical cluster $1/N^{1/d}$ is proportional to the number of atoms in the surface region $n_s \approx R^2$ (R denotes the radius of the cluster) divided by the total number of atoms $n \approx R^3$,

$$1/N^{1/d} \approx 1/R \quad (4)$$

It can be seen that the influence of the surface on the properties of the whole cluster decreases with the relative contribution of the surface atoms, as is to be expected. One would of course expect that formulae of the form of eqn. (1) are applicable for values of R that are very large in comparison with the average atomic distance or lattice constant. It appears, however, that formulae of this kind can often be used with reasonable accuracy for very small clusters starting from $N=10$ or 20 when $N^{-1/3}$ is of the order of 1/2 or 1/3. This is a remarkable result indicating the usefulness of such formulae for interpolating experimental data and, in a more general sense, for bridging the gap between two theoretical disciplines, i.e. quantum chemistry and solid state physics. This may be of large theoretical importance, since the usual computational methods of quantum chemistry and solid-state physics cannot be applied to finite systems having a very large number of atoms. The aim of this paper is to summarize the most important results obtained in this respect and to give examples of formulae of a similar kind from other fields of physics and chemistry. We show

that the existence of such interpolation formulae is not accidental and is related to the very general behaviour of both quantum and classical systems of increasing size.

INTERPOLATION FORMULAE IN OTHER FIELDS OF PHYSICS

The expression for the surface tension of a droplet which shows that the surface tension decreases as $1/R$, where R is the radius of a droplet, is well known (see for example the discussion in ref. 1). The analogy with eqn. (1) is obvious.

Some interesting results were achieved by Weyl at the beginning of this century [28-35]. Weyl showed that asymptotically leading terms in the integrated density of states of the scalar wave equation depend only on the surface of the considered region but not on its shape. The answer to the question of whether one can hear the shape of a drum must, therefore, be answered in a negative sense. For a sufficiently large drum its spectrum does not depend on its shape. It has been also shown (see ref. 36) that it is impossible to hear the style which a cathedral is built (i.e. the curvature of its surface, singularities at the surface, etc.) since the spectrum of the concert does not depend, at least for sufficiently large cathedral, on the surface details. Weyl also considered the spectrum of the electromagnetic waves in a cavity an elastic vibrational problem. All three problems led to the same conclusion: the integrated density states, $I(E)$, i.e. the number of eigenvalues less than a given number E , depends asymptotically (for very large volume, V , or surface, S , for two-dimensional systems) only on V or S and is independent of the form of the boundary region. This result is closely related to the Planck formula [37] for black-body radiation or the Debye T^3 law for specific heat [38] which are valid only for very large volume. The first correction to these formulae for a finite volume proportional to the surface/volume ratio, similarly to the results mentioned above [36]. Analogous results were obtained also for the Stefan-Boltzmann law [36, 39]. We note that deviations from these laws for finite volumes have been observed experimentally [36].

Similar results have also been obtained in other fields of physics, e.g.: acoustics of rooms, the thermodynamic properties of ideal gas in a finite volume, the semiempirical formula for the nuclear binding energy, autocorrelation functions in statistical physics, the Bose-Einstein condensation in thin films and the vibrational contribution to the specific heat of small crystal particles (for a review see ref. 36). Further examples from different fields of physics can be found in refs. 24, 36 and 41-46.

DEPENDENCE OF INTERPOLATION FORMULAE ON $1/N^{1/3}$

As can be seen from the examples given above, the formulae analogous

eqn. (1) appear in both classical and quantum physics and can be found in both non-relativistic and relativistic physics (for the relativistic photon gas see ref. 36). It is obvious that their existence must be related to some general property which is common to all these fields. Regardless of the classical or quantum formulation, we search for the size dependence of the physical properties of a system in a finite volume. The corresponding equations of motion may differ according to the problem solved; it may be the diffusion equation, wave equation, Schrödinger equation or another equation of motion. The unifying point of view can be found by transforming this equation of motion into matrix form within a suitably chosen localized basis set. In the case of clusters and the Schrödinger equation the basis set used could be, for example, the LCAO basis. When increasing the cluster size we can suppose that the matrix elements corresponding to the basis functions at large distances from the surface change negligibly in contrast to those where at least one basis function lies near the surface. As a result, we obtain in all cases a Hermitian matrix eigenvalue problem of the form

$$\mathbf{A}\mathbf{x} = \lambda\mathbf{B}\mathbf{x} \quad (5)$$

where \mathbf{B} is a positive definite "overlap" matrix ($\mathbf{B} = \mathbf{1}$ for the orthogonal basis), and λ can, for example, have the meaning of energy (stationary Schrödinger equation) or the square of the frequency (wave equation). Some matrix elements of the matrices \mathbf{A} and \mathbf{B} change negligibly with the increasing size of the system (we denote this set as a) while the others are surface dependent (set b). The problem (eqn. (5)) can then be partitioned in the form

$$\mathbf{A} = \begin{bmatrix} A_{aa} & A_{ab} \\ A_{ba} & A_{bb} \end{bmatrix}, \quad \mathbf{B} = \begin{bmatrix} B_{aa} & B_{ab} \\ B_{ba} & B_{bb} \end{bmatrix}, \quad \mathbf{x} = \begin{bmatrix} x_a \\ x_b \end{bmatrix} \quad (6)$$

Denoting the number of eigenvalues of eqn. (5) which are lower than a real number μ (the integrated density of states) as $I\{\mathbf{A}, \mathbf{B}; \mu\}$ and using the so-called negative eigenvalue theorem [7,40,47-50], which is closely related to the result of Weierstrass [51], we get

$$I\{\mathbf{A}, \mathbf{B}; \mu\} = I\{A_{aa}, B_{aa}; \mu\} + I\{\tilde{\mathbf{A}}_{bb} - \mu B_{bb}, \mathbf{1}; 0\} \quad (7)$$

Here, the μ -dependent matrix $\tilde{\mathbf{A}}_{bb}$, sometimes called the effective Hamiltonian, equals

$$\tilde{\mathbf{A}}_{bb} = A_{bb} - (A_{ba} - \mu B_{ba})(A_{aa} - \mu B_{aa})^{-1}(A_{ab} - \mu B_{ab}) \quad (8)$$

Without going into detail (see for example refs. 7 and 40) we see that the contribution of the second term in eqn. (7) to $I\{\mathbf{A}, \mathbf{B}; \mu\}$ cannot be larger than the number of the basis functions, n_b , present in the surface region b

$$0 \leq I\{\tilde{\mathbf{A}}_{bb} - \mu B_{bb}, \mathbf{1}; 0\} \leq n_b \quad (9)$$

On increasing the size of the system, the number of basis functions in the region a increases proportionally to the volume V

$$n_a \simeq V \quad (10)$$

while n_b depends on the surface S

$$n_b \simeq S \quad (11)$$

This means, therefore, that the relative contribution of the second surface term in eq. (7) to the integrated density of states cannot be larger than a constant $\times S/V$. The form of the surface is not important here. This result is very general as it does not depend on the values of the matrix elements of the matrix \mathbf{A} and \mathbf{B} and is valid for any problem of the form of eqn. (5). Equation (11) gives the lower and upper bounds to $I\{\tilde{\mathbf{A}}_{bb} - \mu B_{bb}, \mathbf{1}; 0\}$. The actual contribution of the surface term to $I\{\mathbf{A}, \mathbf{B}; \mu\}$ can be considerably smaller. More detailed discussions are given in Refs. 2 and 7. We note that the Ledermann theorem [52] follows from eqn. (7) as a special case.

According to this result, the upper bound to the relative contribution of the surface term to the eigenvalue spectrum is proportional to S/V , in agreement with the closely related results of Weyl. The real dependence of the quantities derived from the eigenvalue spectrum on S/V depends, of course, on their character. This is the reason why some cluster properties depend on $1/N^{1/3}$ (binding energy) while the others have $1/N^{2/3}$ dependence (band width and lower occupied MO). We note that, for small clusters, better agreement with experiment may be achieved if instead of $S/V \simeq 1/N^{1/3}$ the parameter proportion to $S/(V-S)$ is used [44].

USE OF INTERPOLATION FORMULAE FOR BIOLOGICALLY IMPORTANT MACROMOLECULES

Many biologically important molecules like proteins have a quasilinear structure which is ideal for the use of the negative eigenvalue theorem. Because of the quasilinear structure, the interpolation formulae can be written in the form

$$Q(N) = Q(\infty)(1 + c_1/N + c_2/N^2 + \dots) \quad (12)$$

where N is the number of some elementary units (for example, a few amino acids) from which the molecule can be created by some symmetry operation (rotations, translations, etc.) and $Q(\infty)$, c_1 , c_2 , etc. are constants which can be found by fitting experimental data or the results of quantum-chemical calculations.

The formulae of the form of eqn. (12) have been successfully applied to polypeptides [40]. The investigated properties were the π -electron property, the total energy, the dipole moment and the Gibbs free energy.

The interpolation formulae comprise, especially for biologically important macromolecules, a simple, inexpensive and theoretically justified approach which can give interesting results in interpreting experimental data as well as in predicting the size dependence of their physical, chemical and thermodynamic properties.

CONCLUSIONS

Although the actual dependence of the properties of clusters, macromolecules and other finite systems on their size may be complicated, the discussion given above shows that the negative-eigenvalue theorem provides a general argument that the use of interpolation formulae depending on the parameter $1/N^{1/d}$ is a reasonable approximate approach to describing the size dependence of the properties of finite systems. The examples given above show that the interpolation formulae usually lead to very good results for both clusters and polypeptides. It is obvious that further investigation of concrete properties as well as the inclusion of further terms in eqn. (1), depending on the curvature of the surface and its other properties, can give interesting results, especially for clusters, polypeptides and other biologically important macromolecules.

REFERENCES

- 1 H. Muller, Ch. Opitz, K. Strickert and L. Skala, *Z. Phys. Chem. (Leipzig)*, **268** (1987) 625.
- 2 L. Skala, *Phys. Stat. Sol.*, Ser. b, **127** (1985) 567.
- 3 O. Bilek, L. Skala and L. Kunne, *Phys. Stat. Sol.*, Ser. b, **117** (1983) 675; L. Kunne, L. Skala and O. Bilek, *Phys. Stat. Sol.*, Ser. b, **118** (1983) 173.
- 4 L. Skala, *Phys. Stat. Sol.*, Ser. b, **109** (1982) 733.
- 5 L. Skala, *Phys. Stat. Sol.*, Ser. b, **110** (1982) 299.
- 6 L. Kunne, L. Skala and O. Bilek, *Czech. J. Phys.*, Ser. B, **29** (1979) 1030.
- 7 L. Skala, *Czech. J. Phys.*, Ser. B, **27** (1977) 171.
- 8 O. Bilek and L. Skala, *Czech. J. Phys.*, Ser. B, **28** (1978) 1003.
- 9 O. Bilek and P. Kadura, *Phys. Stat. Sol.*, Ser. b, **85** (1978) 225.
- 10 P. Kadura and L. Kunne, *Phys. Stat. Sol.*, Ser. b, **88** (1978) 537.
- 11 H. Muller, *Z. Chem.*, **3** (1963) 369.
- 12 H. Muller, *Z. Chem.*, **12** (1972) 475.
- 13 H. Muller, *Z. Phys.*, Ser. D, **3** (1986) 233.
- 14 B. Delley, D.E. Ellis, A.J. Freeman, E.J. Baerends and D. Post, *Phys. Rev.*, Ser. B, **27** (1983) 2132.
- 15 H.-G. Fritzsche, *Phys. Stat. Sol.*, Ser. b, **143** (1987) K11.
- 16 S. Romanowski, P. Mlynarski, Ch. Opitz and H. Muller, *Wiss. Ztschr. Friedrich-Schiller-Universität Jena, Naturwiss. R.*, **36** (1987) 539. H. Muller, L. Skala, Ch. Opitz and K. Strickert, *Wiss. Ztschr. Friedrich-Schiller-Universität Jena, Naturwiss. R.*, **36** (1987) 531.
- 17 C. Brechignac and Ph. Cahuzac, *Z. Phys.*, Ser. D, **3** (1986) 121.
- 18 A. Herrman, E. Schumacher and L. Woste, *J. Chem. Phys.*, **68** (1978) 2327.
- 19 L. Skala and H. Muller, *Lecture Notes in Physics*, Vol. 269, Springer, Berlin, 1986, p. 144.

- 20 A.W. Castleman and R.G. Keesee, *Z. Phys.*, Ser. D, **3** (1986) 167.
- 21 H. Muller, Ch. Opitz, S. Romanowski and L. Skala, *Phys. Stat. Sol.*, Ser. b, **148** (1988) K1.
- 22 W. Vogelsberg, H.-G. Fritzsche and E. Muller, *Phys. Stat. Sol.*, Ser. b, **148** (1988) 155.
- 23 R.D. Etters, K. Fluzchick, R.P. Pan and V. Chandrasekharan, *J. Chem. Phys.*, **75** (1981) 929.
- 24 R. Kubo, A. Kawabata and S. Kobayashi, *Ann. Rev. Mat. Sci.*, **14** (1984) 49.
- 25 J. Koutecky and P. Fantucci, *Chem. Rev.*, **86** (1986) 539.
- 26 L.D. Kunne and H. Muller, *Z. Chem.*, **26** (1986) 345.
- 27 J. Schwinger, *Phys. Rev.*, Ser. A, **22** (1980) 1827.
- 28 H. Weyl, *Göttinger Nachr.*, (1911) 110.
- 29 H. Weyl, *Math. Ann.*, **71** (1912) 441.
- 30 H. Weyl, *J. f. Reine Angew. Math.*, **141** (1912) 1.
- 31 H. Weyl, *J. f. Reine Angew. Math.*, **141** (1912) 163.
- 32 H. Weyl, *J. f. Reine Angew. Math.*, **143** (1913) 177.
- 33 H. Weyl, *Rend. Circ. Mat. Palermo*, **39** (1915) 1.
- 34 H. Weyl, *Bull. Am. Math. Soc.*, **56** (1950) 115.
- 35 H. Weyl, in K. Chandrasekharan (Ed.), *Gesammelte Abhandlungen*, Vol. I, Abhdlg, Springer Berlin, 1968, No. 13, 16-19, 22.
- 36 H.P. Baltes and E.R. Hilf, *Spectra of Finite Systems*, Bibliographisches Institut AG, Zurich 1976.
- 37 M. Planck, *Verhdl. Deut. Phys. Ges.*, **2** (1900) 202; *Physikalische Abhandlungen und Vorträge*, Vol. 3, Braunschweig Vieweg, 1900, p. 125.
- 38 P. Debye, *Ann. Phys. (Leipzig)*, **39** (1912) 789.
- 39 L. Boltzmann, *Ann. Phys. (Leipzig)*, **258** (1884) 291.
- 40 L. Skala and P. Pancoska, *Chem. Phys.*, **125** (1988) 21.
- 41 V.R. Pandharipande et al., *Phys. Rev. Lett.*, **50** (1983) 1676.
- 42 J. Myers and W.J. Swiatecki, *Nucl. Phys.*, **81** (1966) 1.
- 43 N.M. Hugenholtz and D. Pines, *Phys. Rev.*, **116** (1959) 489.
- 44 W.C. Stwalley and M. de Llano, *Z. Phys.*, Ser. D, **2** (1986) 153.
- 45 H.R. Lee et al., *Phys. Rev.*, Ser. B, **39** (1989) 2822.
- 46 H. Neuberger and T. Ziman, *Phys. Rev.*, Ser. B, **39** (1989) 2608.
- 47 P. Dean, *Rev. Mod. Phys.*, **44** (1972) 127.
- 48 J. Hori, *Spectral Properties of Disordered Chains and Lattices*, Pergamon, Oxford, 1968.
- 49 J. Ladik et al., *Int. J. Quantum Chem.*, **29** (1986) 597.
- 50 O. Litzmann and P. Rosza, *Proc. R. Soc.*, **85** (1965) 285.
- 51 J. Jeffreys and B.S. Jeffreys, *Methods of Mathematical Physics*, Cambridge University Press Cambridge, 1946, p. 127.
- 52 W. Ledermann, *Proc. R. Soc.*, Ser. A, **182** (1944) 362.