

Interpolation formulae for describing size dependence of properties of clusters and finite systems

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Abstract. Size dependence of stationary as well as non-stationary properties of clusters and finite systems is discussed and simple interpolation formulae for the properties of finite systems together with examples of their use for clusters and other systems are given and discussed.

1. Introduction

The importance of the investigation of the size dependence of physical properties of finite systems is obvious. Real physical systems have finite dimensions and their properties depend on their size. This dependence can be observed in many experiments and represents important information which should be theoretically analyzed. It is obvious that this problem is very general and we cannot present here all its aspects and the large amount of experimental results from various fields of physics and chemistry. Instead, we will present here some general remarks and a few applications from the physics and chemistry of clusters.

The importance of the surface of finite systems is given by the boundary conditions which appear in the corresponding equations of motion. These equations can be classical equations of motion, wave equation, Schrödinger equation, classical or quantum Liouville equation and others. The size dependence of time independent, stationary, properties is in general easier to investigate and more results are known. For this reason, we will discuss first stationary properties with some applications from physics and chemistry of clusters. At the end of the paper, we will discuss briefly non-stationary properties.

2. Stationary properties of clusters and thin films

There are numerous examples showing that the size dependence of physical and chemical properties of atomic clusters, thin films 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 respected. To be more concrete, we discuss first the cluster properties. The shape of the cluster of the concrete form of the surface boundary conditions do of course play 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, 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 the dimensions 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 (1) were successfully applied to different electron, geometrical and thermodynamical properties of various clusters and thin films. The interpolated quantities were the electron binding energy [1–15], band width [2, 4–5], lowest occupied MO [2, 4–5], ionization potential and work function [13, 16–20], lattice constant [1], distance of the CO molecule from the surface of the solid [1], entropy [1], free energy [1], position of the Mie resonant absorption [1], specific resistance of thin films [1], contact potential [21], surface stress and tension [22] and other properties [1, 23–27]. The first example we shall give is the formula for the ionization potential of Na clusters.

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

Starting from $N = 5$ the formula (2) gives a reasonable description of the experimental data with the error 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 [1]

$$\Delta S^{\text{Al}}(R)/k = 7.8/R \text{ (R in \AA, } k\text{-Boltzmann constant)}. \quad (3)$$

This formula is in good agreement with experimental data starting from $R \sim 15 \text{ \AA}$.

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

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

We see that the influence of the surface on the properties of the whole cluster decreases with the relative contribution of the surface atoms as it is to be expected. One would of course expect that the formulae of the form (1) are applicable for R very large in comparison with the average atomic distance or lattice constant. It appears, however, that the formulae of this kind can often be with a reasonable accuracy used for very small clusters starting from $N = 10$ or 20 when $N^{-1/3}$ is of the order $1/2$ 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 — quantum chemistry and solid state physics. This may be of considerable theoretical importance since the usual computational methods of quantum chemistry as well as of solid state physics cannot be applied to finite systems with a very large number of atoms. In the following paragraphs, we summarize the most important results in this respect and give examples of formulae of a similar kind from other fields of physics and chemistry. We will show that the existence of such interpolation formulae is not accidental and is related to a very general behaviour of both quantum and classical system with increasing size.

3. 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 e.g. discussion in [1]). The analogy with Eq. (1) is obvious.

A few 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 if one can hear the shape of a drum must be therefore answered in a negative sense. For a sufficiently large drum its spectrum does not

depend on its shape. It has been also shown (see [36]) that it is impossible to hear the style of a cathedral in which it 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 a sufficiently large cathedral, on the surface details. Weyl considered also the spectrum of the electromagnetic waves in a cavity and elastic vibrational problem. All three problems lead to the same conclusion: The integrated density of states $I(E)$ i. e. the number of eigenvalues of the problem 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 existence of the Planck formula [37] for the black body radiation or Debye T^3 law for the specific heat [38] which are valid only for very large volume. The first correction to these formulae for a finite volume is proportional to the ratio surface/volume 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 can be observed experimentally (see [36]).

In other fields of physics similar results were obtained, too. We should mention the acoustics of rooms, thermodynamic properties of ideal gas in a finite volume, semiempirical formula for the nuclear binding energy, autocorrelation functions in statistical physics, Bose-Einstein condensation in a thin film and vibrational contribution to the specific heat of small crystalline particles (see review [36]). Further examples from different fields of physics can be found in [24, 36, 41–46].

4. Dependence of interpolation formulae on $1/N^{1/3}$

As we see from the examples given above, the formulae analogous to (1) appear both in classical and quantum physics and can be found both in non-relativistic and relativistic physics (for the relativistic photon gas see [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 physical properties of a system in a finite volume. The corresponding equations of motion may be different depending on 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 transforming this equation of motion into the matrix form in a suitably chosen localized basis. In case of clusters and Schrödinger equation it may 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 distance from the surface change negligibly in contrast to those where at least one basis

function lies near the surface. As a results, we get in all cases a hermitian matrix eigenvalue problem of the form

$$Ax = \lambda Bx, \quad (5)$$

where B is a positive definite "overlap" matrix ($B = 1$ for the orthogonal basis). λ can have, for example, the meaning of energy (stationary Schrödinger equation) or the square of the frequency (wave equation). Some matrix elements of the matrices A and 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 (5) can be then partitioned into the form

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

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

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

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

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

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

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

Increasing the size of the system, the number of the basis functions in the region a increases as the volume V

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

while n_b depends on the surface S

$$n_b \sim S. \quad (11)$$

It 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 matrices A and B and is valid for any problem of the form (5). Equation (9) gives the lower and upper bound to $I\{\tilde{A}_{bb} - \mu B_{bb}, 1; O\}$. The actual contribution of the surface term to $I\{A, B; \mu\}$ can be considerably smaller. More detailed discussion can be found in [2, 7]. We note that the Lederer theorem [52] follows from Eq. (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 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. It is the reason that some cluster properties depend on $1/N^{1/3}$ (binding energy) while the others have $1/N^{2/3}$ dependence (band width, the lowest occupied MO). We note that for small clusters better agreement with experiment may be achieved if instead of $S/V \sim 1/N^{1/3}$ the parameter proportional to $S/(V-S)$ is taken [44]. We note also that for fractal surfaces the number of atoms at the surface is proportional to its fractal dimension df , $S \sim N^{df}$, so that $S/V \sim 1/N^{3-df}$. In such a case, the exponent in the interpolation formula (1) can be different from $1/3$ or $2/3$.

5. Note on the interpolation formulae for quasilinear 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 operations (rotations, translations, ...) and $Q(\infty)$, c_1 , c_2 , ... are constants which can be found by fitting experimental data or results of quantum chemical calculations.

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

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

6. Introducing temperature into the interpolation formulae

We assume that the interpolation formula

$$Q_n(N) = Q_n(\infty)(1 - c_n/N^{1/d}) \quad (13)$$

can be used for any state n with the energy E_n of the finite system with N atoms or other units. Assuming the validity of the Gibbs statistical distribution the average value of the quantity Q at temperature T equals

$$Q = \sum_n Q_n \exp(-E_n/kT) / \sum_n \exp(-E_n/kT). \quad (14)$$

If $E_n/kT \ll 1$ we can use the expression $\exp(-E_n/kT) = 1 - E_n/kT$ and derive the following approximate size and temperature dependence of Q

$$Q(N) = A - B/N^{1/d} + [C - D/N^{1/d}]/kT, \quad (15)$$

where A , B , C and D are constants. The expression of this form was successfully applied to the CD spectra of polypeptides [53].

7. Non-stationary properties

In case of non-stationary properties, the problem is complicated by the existence of a further "degree of freedom", time. This complicates both the theoretical analysis and experimental investigation (necessity to perform time resolved experiments). The amount of information in this respect is therefore limited.

First we consider the solution of the Schrödinger equation

$$H \psi_n = E_n \psi_n \quad (16)$$

with time independent hamiltonian H . A general solution of the time Schrödinger equation equals

$$\psi(t) = \sum_n c_n \exp[E_n t/(i\hbar)] \psi_n \quad (17)$$

and the average value of a time independent operator L equals

$$\bar{L} = \sum_{n,m} c_n^* c_m \exp[(E_m - E_n)t/(i\hbar)] L_{nm}, \quad (18)$$

where

$$L_{nm} = \int \psi_n^* L \psi_m dt. \quad (19)$$

The size dependence of \bar{L} appears in the time dependent part of (19) through $E_m - E_n$ and the matrix elements L_{nm} . Also the coefficients c_n given by the initial conditions are different for different size of the system. The

Where F is a matrix of rate constants, the propagator for the infinite linear chain equals [54]

$$\psi_{np}(t) = (2\pi)^{-1} \int_{-\pi}^{\pi} e^{in\theta} e^{-ip\theta} e^{2F(-1 + \cos\theta)t} d\theta = e^{-2Ft} I_{n-p}(2Ft), \quad (25)$$

where I is the modified Bessel function. For a finite linear chain we get [56]

$$P_{np}(t) = \sum_{k=0}^{N-1} h_n^{(k)} h_p^{(k)} \exp(\lambda_k t), \quad (26)$$

where λ_k and $h_n^{(k)}$ denote the eigenvalue and the n -th component of the corresponding eigenvector of the matrix F . We see that the result (26) is similar to (23) except for the missing imaginary unit in the exponential. This is characteristic for the transition from the coherent to incoherent motion. Analogous results can be obtained also for the Liouville equation [55].

Theory of the time resolved spectroscopy of the photosynthesis systems shows that, similarly to the stationary properties discussed above, an important parameter is $1/N$, where N denotes the total number of active molecules in photosynthetic unit [57]. More results for the fluorescence intensity, the corresponding quantum yield and other quantities can be found in [57–58].

We have seen a few concrete examples of the size dependence of time dependent properties of finite systems. In more general cases, the results are analogous to those given above.

8. Conclusions

Although the actual dependence of the properties of clusters, thin films, linear 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 interpolation formulae depending on the parameter $1/N^{1/d}$, where d is usually 1, 2, 3 but can be also a small non-integer, are reasonable approximate approaches for describing the size dependence of properties of finite systems. The examples given above show that the interpolation formulae lead to usually very good results. It is obvious that further investigation of concrete properties as well as the inclusion of further terms into the expansion (1) depending on the curvature of the surface and its other properties can give interesting results.

combination of these factors complicates the analysis. In some cases, the problem can be simplified.

For example, the average energy equals

$$E = \sum_m |c_m|^2 E_m. \quad (20)$$

This result is similar to the expression for the binding energy in the analytic cluster model [6–8]. Therefore, except for the dependence on initial conditions, a similar size dependence of E as for the binding energy can be expected.

A special importance play propagators i.e. the response of the system to a localized excitation at $t = 0$. For example, the propagator of the Schrödinger equation for the infinite linear chain equals [54]

$$\psi_{np}(t) = 1/2\pi \int_{-\pi}^{\pi} e^{in\theta} e^{ip\theta} e^{-i/n \cdot 2V \cos\theta t} d\theta = (-i)^{n-p} J_{n-p}(2V \cos\theta t), \quad (21)$$

where J is the Bessel function. $|\psi_{np}(t)|^2$ gives the probability of finding the excitation at time t at size n if the excitation at $t = 0$ was localized at site p ($|\psi_{np}(0)|^2 = \delta_{np}$). For general initial conditions, the solution has the form

$$\psi_n(t) = \sum_p \psi_p(0) \psi_{np}(t). \quad (22)$$

For a finite linear chain with N atoms we get [54]

$$\psi_{np}(t) = 2/(N+1) \sum_{k=1}^N \sin[nk\pi/(N+1)] \sin[pk\pi/(N+1)] \times e^{1/(i\hbar) 2V \cos[k\pi/(N+1)]t}. \quad (23)$$

The comparison of Eqs. (23) and (21) shows that the size dependence of the propagator (23) is mathematically equivalent to the problem of replacing the integration by a discrete sum.

Similar conclusions can be drawn also for the incoherent and partially coherent motion of the excitation. For example, for the Pauli kinetic equation

$$dP_n/dt = \sum_n F_{nn}, P_n, \quad (24)$$

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