

## Universal equation of state for atoms: Vanderwaals-Maxwell-type phase-transition between hydrogen- and antihydrogen-states in neutral H.

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**Abstract.** Macroscopic  $P(V)$  diagrams are consistent with microscopic  $U(r)$  diagrams, with  $U$  an (internal) energy of type  $1/r$ , where  $r$  is a particle separation. If a universal equation of state (UEOS) for atoms exists,  $P(V)$  or  $U(r)$  diagrams can be used with the Vanderwaals-Maxwell binodal and spinodal. This reveals the energy dependence of an atom upon size variations and the corresponding intra-atomic phase-transition. We show that the H Lyman ns-series indeed provides evidence for *an intra-atomic phase-transition*. We promote Bohr  $1/n^2$  theory to *an ideal atom theory*, with atomic size varying as  $r=n^2r_0$ , wherein only the Bohr radius  $r_0 = \hbar^2/\mu e^2$  and  $n$ , the principal quantum number, are needed. We detect a critical point for a phase-transition in H for  $n$  between 5 and 6, if the Bohr Rydberg  $109678.7737 \text{ cm}^{-1}$ , the H ground state energy, is used as the asymptote. Unlike bound state QED, we associate this phase-transition with a shift *from an atom (hydrogen)- to an antiatom (antihydrogen)-state*. This symmetry breaking effect leads to chiral behavior, in line with our previous results from atomic line and molecular band spectra. A *natural internal  $H \leftrightarrow \bar{H}$  phase-transition*, if real, must weigh heavily on ongoing CERN-AD *artificial anti-hydrogen* experiments. This result may well be the missing link to understand the macro- and microscopic behavior of neutral matter and justifies the further search for a UEOS.

Keywords: universal equation of state (UEOS), Vanderwaals, Maxwell, binodal, spinodal, Bohr theory, antihydrogen, chiral symmetry breaking, phase-transitions, bound state QED

### Introduction

A recent study [1] of analyticity properties of the spinodal and the problems connected with the existence of a UEOS (Universal Equation of State) prompted us to review some earlier conclusions on the matter [2]. Unifying macroscopic behavior of many *interacting* particle systems with microscopic behavior of a single particle or unit system of natural observable systems is an important and challenging task in science at large (physics, chemistry, biology...). The standard classical, logical and self-explanatory viewpoint is that the most important difference between macro- and microscopic worlds stems from *inter-particle interactions* and from *statistical effects* (partition functions, distribution laws) *both believed to have vanished in the simplest system imaginable, the single unit particle*. For decades, this hypothesis has played a major role in the development of theories for a variety of disciplines (mean-field theory) but *its absolute validity remains to be proved, which means that it must be formulated analytically using first principles only*. Classical macroscopic kinetic gas theory uses molecules as units and focuses on their individual properties (mass  $m$  and velocity  $v$ , measurable by means of by macroscopic observables pressure  $p$  and density  $d$ , since  $v=(3p/d)^{1/2}$ ). The history of physics and chemistry is full of attempts to solve the intriguing *analytical* relation between the macroscopic and microscopic world, *whereby the universal function (UEOS, universal equation of state) remains to be found*. With the ideal gas law and its extensions due to Vanderwaals, one tries to intrude *into the characteristics of the unit particle on the basis of macroscopic evidence*. Diatomic molecules  $XY$  consist of two (different) atoms  $X$  and  $Y$ , a binary mixture with fixed composition,  $X_2$  is a cluster of 2 atoms  $X$ . The macroscopic aggregate of 1 mole of molecules is a cluster of  $N$  molecules  $X_2$  or  $2N$  atoms  $X$ , where  $N$  is Avogadro's number. *The ultimate, critical and still missing link, however, is the  $P, V$  diagram for the microscopic world, i.e. for the single atom instead of the single molecule and the detection as well as the analytical description of any intra-atomic phase transition, if it would exist*. We try to identify such an intra-atomic phase-transition by making advantage of the fact that a *macroscopic  $P, V$  diagram* has the potential of being also, at least theoretically, the equivalent of a *microscopic  $U, r$  diagram*, whereby  $U$  is *some* energy of type  $1/r$ , with

r a measure for a size of *some* system or *some* distance between 2 particles. Trying to define the nature of the microscopic energy  $U$ ,  $r$  is not straightforward.

## Phenomenology of the continuous transition between micro- and macro-world

Knowledge about intermediate cases between macro- and micro-world is of interest and it is important to bridge this macro-micro-gap in a *continuous* way. Let us define the absolute stable unit as  $X$ , *the atom*, and the degree of clustering by suffix  $n$ . The starting point, the absolute micro-world, is then described by unit  $X_1$ . If it is impossible to study *the single atom*, we study a larger number  $N$  of atoms  $X_1$ , say  $NX_1$ . The next level, in terms of atoms in the unit, is *the diatomic homonuclear molecule*  $X_2$ , which played an important role in kinetic gas theory for  $NX_2$  systems (see Introduction) but also in quantum theory (Planck-Einstein theory of specific heat) for micro-system  $X_2$ . Work on more complex clusters  $X_3$  indicates that double well or Mexican hat type potentials are also required to understand this clustering process [3]. This same type of potential is correlated at large with (chiral) symmetry breaking in elementary particle and atomic physics (*single particle level*  $X_1$ ) and to the behavior of *chiral* molecules (*two or more particle level*  $X_2$  and  $X_4$ , whereby the  $X_4$  case relates to polyvalent atoms and *non-homogeneous* mixtures of atoms). At the homogeneous *many-molecule level*  $NX_2$ , essentially the same but slightly distorted Mexican hat potentials appear but have, since the 19<sup>th</sup> century, been called *binodals* (see further below). This terminology stems from Vanderwaals-Maxwell theory, needed to explain macroscopic phase-transitions (such as liquid-gas). Hence, *phase-transitions within and between particles seem to be very similar, which justifies the search for a UEOS*.

Theoretically, the most interesting case is when *inter-particle forces* are determined by *intra-particle force(s)*, responsible for the stability within a single unit. Then, the above hypothesis can be quantified in a consistent and satisfactory way. Finding an analytical universal function, applicable to and obeyed by both macro- and microscopic world, is an ever-continuing goal for scientists in many disciplines. The inverse argument is that *homogeneous* aggregates of particles show *particle-specific* transitions between aggregation states (solid-liquid, liquid-gas, solid-gas...), *the characteristics of which must be hidden already in the properties of the single neutral unit particle*<sup>1</sup>. Despite many difficulties [1,2,4], it is plausible to assume that a UEOS indeed exists on the basis of two straightforward arguments.

### (a) Ionic aggregates $(AB)_n$

First, there is the apparent similarity between the EOS (equation of state) for ionic solids  $(AB)_n$  of Madelung-Coulomb type and the PEC (potential energy curve) for the unit, the ionic bond  $AB$ , which is of Born-Coulomb type [2,4]. The minimum in the EOS for *solids*  $(AB)_n$  can be assessed from *compressibility measurements*, whereas the minimum in the PEC for the *ionic bond*  $AB$  can be extracted from its spectrum. In essence, this similarity between the two functions for the macroscopic and microscopic worlds is at the basis of trying to unify *analytically* equations of state (EOSs), valid for *many* particle systems, with universal potential functions (UPF), valid for a *single* particle. *It is very clear that in this case the Coulomb force between particles (charge conjugated ions) within the unit is the unifying element for the EOS of the aggregate (crystal)*. This is in line with recent conclusions about the role of the Coulomb potential in chemical bonding [4].

Many more complex potentials are available [1,2,4,5] but not all are performing equally well [1,5], pending their analytical form. Various potentials were proposed with the intimate prospect of being valid for the macroscopic world as well (see reviews [1,2,4]). It is believed, however, that the Coulomb potential is too simple a function to accommodate for the phenomena observed in both the micro- and macroscopic world for all types of bonds but this need not to be true [4]. So, the search for better functions, and their analytic behavior at critical points, is still going strong. According Brosh, Makov and Shneck [1], a good analytical UEOS is

<sup>1</sup> This would be an illustration of *ab uno disce omnes* (Vergil, The Aeneid, II 65)

that of Vinet et al. [6], resulting from an earlier universal function suggested by Rose et al. [7]. Universal functions as those in [6-7] are supposed to apply to a variety of domains but must also meet the stringent condition to be applicable in both macro- and microscopic domains. UPFs must be useful for complex particle systems and single particles, ranging from elementary particle to nuclear and molecular physics (chemistry) to applied physics and chemistry as well and, therefore, from the macro- to the microscopic world. *This means that the condition for universality must be understood and fulfilled from first principles. However, we must realize thereby that, to make observations, we are doomed to work continuously and exclusively in a macroscopic world<sup>2</sup>.*

A drawback of Vinet-Rose-type functions [6-7], *essentially covalent functions*, is that an *extra ionic term* is needed, as remarked in [1], to be applicable also for the generic and *simpler* case of ionic bonds (ionic aggregates) of type  $(AB)_n$ . In [1], it was argued that this correction term does not play an important role with respect to universality, *which we feel this may be a wrong argument*. For instance, looking at the straightforward universality in the ionic case, the need for an *extra ionic correction term in an already ionic universal function* seems strange. In fact, we showed that the choice of the *binding energy* for the unit system is critical to unify the spectral behavior of various types of bonds, e.g. covalent and ionic, in order to remove the so-called *spectroscopic gap* between the two [8]. *This artificial gap is the direct result of a wrong asymptote choice*. This is a serious problem for retracing universal behavior, since one cannot intermix, rather arbitrarily, totally different asymptotes (like covalent and ionic [8]). One must adhere to a single unique and well-defined asymptote in order to be able to speak of universal behavior, as I pointed out a long time ago [8]. This conclusion was apparently overlooked by Vinet et al. [6] as well as by Rose et al. [7] but seems to be confirmed by Brosh, Makov and Shneck [1]. Shifting rather arbitrarily from the covalent to ionic asymptote means that an ionic-covalent phase-transition is introduced artificially, *if not arbitrarily or intuitively*. This phase-transition between an atomic and an ionic system is *not continuous* in terms of asymptotes as it involves a charge-transfer of type  $X+Y \leftrightarrow X^+ + Y^-$ , which affects the mode of the interaction, i.e. from ionic to non-ionic (atomic). This can be accompanied by large asymptote shifts, pending the difference between X and Y [8].

This important problem of choosing *the best bond energy* to arrive at universality [2,8] was at least recognized in [1] for the more specific context of testing the analyticity requirement for the spinodal, describing that part of the locus in the P, V diagram where the originally homogeneous phase becomes very sensitive to small fluctuations. The universal function is largely determined by its asymptote. If the function is really universal, scaling each function with this asymptote must invariantly reproduce *the same universal numerical function* [4] much like Vanderwaals reduced equation of state (see below). Similarly, the spectroscopic constants can be unified [8] just by redefining the Sutherland parameter, first introduced by Varhnsni [5]. This important parameter for molecular spectroscopy and its underlying universal function is, in turn, a simple scalable function of that asymptote [1,2,4,5,8]. In terms of Helmholtz free energies F, the asymptote problem can be stated generally as [1]

$$F(P, V_0) - F(P, V_\infty) = F_0 \quad (1)$$

whereby  $F_0$  is the asymptote (the reference *free energy*) needed to describe the system and to check, eventually, for the occurrence of phase-transitions in the system. Free energy  $F_0$  has only to do with the *smooth or continuous* expansion (contraction) process from  $V_0$  to  $V_\infty$ , or, eventually in the micro-world, from  $r_0$  to  $r_\infty$ . This means in particular that phase transitions, *having nothing to do with this continuous expansion or contraction process* (such like a *discrete* redistribution of charges by charge transfers) cannot be allowed if they occur in the region between  $r_0$  and  $r_\infty$ . In concreto, the *ideal* ionic Coulomb potential  $-e^2/r$  would not tolerate different kinds of phase-transitions somewhere between  $r_0$  and  $r_\infty$ . In search for universal behavior of Coulomb type, an *atomic* asymptote with energy  $-U_{XX}$  cannot be used for an *ionic* interaction [2,4,8]. Only an ionic Coulomb asymptote with energy of type  $-U_{X+Y}$  is to be recommended in a process like (1) if an ionic model holds for

<sup>2</sup> Today, single particle measurements are only possible for ions (not neutral particles) but the set-up is extremely complex. The apparatus is so sensitive that it is almost impossible to avoid environmental noise.

the size variations covered by (1). *As a matter of fact, ionic asymptotes are much more suited to rationalize the universal behavior of individual bonds, described by their molecular spectroscopic constants [2,4,8].* For  $F_0$ , producing a constraint for UEOS by means of (1), a similar conclusion was reached in [1] but on different grounds.

(b) *Dimensional analysis*

The macroscopic energy PV in kinetic gas theory (from which the ideal gas law derives) shows that the force exerted by the particles on the wall of the pressure chamber derives from their mass, their average (microscopic) velocity as well as from the number of colliding particles in a unit time. A change in T gives a shift in the hyperbolic P, V diagrams, *all reflecting the behavior of an ideal gas without an internal phase-transition.*

Classical macroscopic energy PV is a force *divided* by a unit surface (length<sup>2</sup>) and multiplied by a volume (length<sup>3</sup>). For any inverse power *force*  $1/r^2$  (length<sup>-2</sup>), the result for product PV is always an energy U of type  $1/r$  (if r is commensurate with the characteristic *length* for the system). For unit system species H (the prototype for atoms), the classical kinetic energy U of type  $\frac{1}{2}m_H v_H^2$ , commensurate with a thermal energy  $kT_H$ , leads invariantly to a U(r) diagram of hyperbolic type also. If true, this ascertains that the first candidate for a universal function of the *ideal* kind (like *the ideal gas law*) can be a simple  $1/r$  interaction law as Coulomb's, exactly as we suggested recently [4]. The Coulomb law itself is also the starting point of the Bohr model for atom H. Then, if the deviations from the ideal gas law PV=RT (wherein the observed macroscopic phase-transitions are missing) can be understood with adaptations of Vanderwaals-Maxwell type, it can be anticipated that similar corrections must be introduced for understanding phase-transitions in the micro-world or within atoms, i.e. deviations from the inverse power law like Coulomb's, *which then serves as an ideal law of interaction.*

### Can there be a phase-transition within a unit system like H?

*The generic obstacle in the transition from a macro- to a micro-system is the concept of states of aggregation. A single unit of matter, when isolated, can never show the properties of changes in the state of aggregation, so clearly visible when a macro-system is studied. The single unit can only be subject to changes in external conditions (temperature, pressure...) which forces one to look for phase-transitions, if any, within the unit system itself. Then this internal phase transition, if detectable, can be at the root of observed changes (in the state of aggregation) in the corresponding macro-system.*

However, since neutral species H can be looked upon as a stable Coulomb system, e.g. the electron-proton bond, with a static Coulomb energy varying as  $-e^2/r$ , it is obvious that, if an internal phase-transition is possible in unit H, this species shall have to be looked upon as a binary mixture of two different phases, say  $H_\alpha$  and  $H_\beta$ . Partition functions are available from the *molar* composition of this binary mixture, say x for phase  $H_\alpha$  and (1-x) for phase  $H_\beta$ , obeying  $1 = x + 1-x$ . Then, a *non-ideal* behavior of neutral species H, with internal composition

$$H = xH_\alpha + (1-x)H_\beta \quad (2)$$

subject to size variations can only show, in the Vanderwaals-Maxwell view, *when some physical or internal physical properties of  $H_\alpha$  are different from those of  $H_\beta$ . The experimental detection of a phase-transition connected with (2) is then crucial* [9]. Then, in the classical macroscopic view, phase  $H_\alpha$  would be linked with the liquid state, whereas  $H_\beta$  would refer to the gaseous state, in coexistence with the liquid (or vice versa). This working hypothesis suffices to make the further analysis consistent.

Based upon additional arguments along lines (a) and (b) above, we recently even gave evidence for considering the simple Coulomb potential itself as a serious candidate for being a truly universal function for all types of molecules, including covalent molecule  $H_2$  [4]. But, if the *inter-atomic* Coulomb function were really universal, this unconventional but nevertheless appealing solution has a price: *we should concede that a natural atom could somehow transform naturally into a charge-inverted anti-atom* [4]. This is the only way to smuggle in pseudo-ionic Coulomb attraction

into covalent bonds like H<sub>2</sub> [4]. One can argue whether or not this is too high a price. But, to be consistent and to make sense [10], this rather unconventional view directly implies that the available atomic H line spectrum should provide evidence for a phase-transition between a hydrogen- and an antihydrogen-state, to be interpreted with deviations from a pure Coulomb law (a field effect), as suggested in (2). To the best of my knowledge, this has never been reported in the post-Bohr era, not even in the context of highly accurate bound state QED where most corrections are of *non-classical type*. Surprisingly, spectral evidence for *mirror symmetry* within the hydrogen species exists [10]. This brings us to the problem of phase-transitions in general and in hydrogen in particular as sketched in (2) using the prescription of this physical process provided by the classical 19<sup>th</sup> century the Vanderwaals-equation. We just have to find a way to realize this.

We could promote Bohr  $1/n^2$  theory to an *ideal atom law* (the ideal rotator), to remain in line with the terminology of classical thermodynamics and the kinetics based macroscopic ideal gas law. The justification is that original *microscopic* Bohr  $1/n^2$  theory for H gives errors of  $10^{-7}$  to  $10^{-8}$  for terms, an accuracy much better than that of most macroscopic measurements. We must then find quantitative evidence for critical points (critical n-values) in the internal energy, *when the size of H is altered*. If an atomic UEOS-thesis is valid, the observed U(r) diagram for H must be similar to the classical P (V) diagram for the macroscopic phase-transition of the homogenous hydrogen gas when compressed to transform in the homogeneous liquid. *By extension and by using experimental data on the compression of single species H, we find that there is indeed a phase-transition within H during such a compression*. This phase-transition can, be it not exclusively, be understood with a reversible hydrogen-antihydrogen (H $\leftrightarrow$ H̄) transition like in (2), for which we already presented evidence elsewhere [10]. We can now explicitly illustrate this remarkable natural phase-transition *with its binodal for the simple electron-proton bond*. This result is in line with the classical Vanderwaals-Maxwell interpretation of macroscopic phase-transitions in homogeneous and in binary systems. Its possible impact on the ongoing CERN-AD experiments on *artificially produced* antihydrogen [11-13] is discussed.

### Theory: from a macro- to a micro system of neutral particles (units of matter)

*Classical transition from macro- to micro-systems using Avogadro's number as a scale factor. Consequences of particle models.*

Having collected sufficient arguments to unify our view about the micro-system, the neutral matter unit and the macro-system, consisting of aggregates of these matter units, we must look for analogies in their analytical treatment in order to arrive at a UEOS.

We skip the details of the full thermodynamic treatment, including the partition functions and distribution laws and including the unit based analytical treatment using mass, pressure and velocity. We start with the ideal gas law and the Vanderwaals equation, as the two are related to the virial (and its coefficients). The classical ideal gas law is the standard equation of state (EOS)

$$PV=RT=NkT \quad (3)$$

where k is the Boltzmann constant, and it is valid, in this form, for one mole of or for N neutral *non-interacting* molecules or atoms. The law led to Avogadro's number and Kelvin's absolute temperature, using a classical kinetic model, based upon a *material point description* for (non-interacting) particles.

To understand deviations from (3), the *material point-description* had to be abandoned, since it does not take into account the dimensions of a neutral unit (molecule, atom). Using a sphere-like model instead, elementary corrections to the ideal gas law or EOS (1) are easily found (we leave out important more recent solutions like Flory and mean-field theory...).

Vanderwaals' 1873 seminal refinement of (3) led to a more general form

$$(P+a/V^2)(V-b) = RT=NkT \quad (4)$$

which is one of the major achievements of classical physics [14]. The ideal gas law, EOS (3), states that for a given temperature T, *P varies inversely with V*: a higher external pressure P leads to

a smaller volume  $V$  for a mole of units of a homogeneous ideal gas and vice versa. In reality, gases, when being compressed, show an easily observable phase-transition, which sets in at the condensation point, after which the gas gradually goes over in a liquid, *without changing the nature or the identity of the neutral units (atoms, molecules) of the originally homogeneous gas*. Macroscopic evidence led Vanderwaals to (4) to cope with observed liquid-gas phase-transitions. EOS (4) is obeyed well by experiment, although refinements are still needed, such as Van Laar's formula for *volume b* (4). Transitions between different states of aggregation can conveniently be called order-disorder transitionS and, as such, are of fundamental importance in a number of applied sciences.

As early realized by Maxwell, the impact of (4) was dramatic, especially when it appeared that Vanderwaals constant  $a$  is also related to the *dielectric constant*. The search for a UEOS for an aggregate of neutral units (atoms, molecules) goes on for decades [2,4] for a variety of reasons. For instance, EOS (4) leads to a *numerical reduced Vanderwaals equation*, referring in a universal way to *critical points* in any macro-system and to *the law of corresponding states*. It also led Maxwell to an underlying function of state, determining qualitatively the internal mechanics of phase-transitions not only in homogeneous aggregates but also in non-homogeneous binary mixtures, all relying on (4). Binodals and spinodals appear, which are fundamental to understand analytically a variety of observed critical phenomena, especially phase-transitions in particle aggregates of various types (solid, liquid, gas states, non-homogeneous) [1]. Given the fact that the Helmholtz free energy should be analytic at the spinodal, an UEOS like Vinet's [6] or a pseudospinodal EOS like Boanza's [15] can be tested for analyticity at this locus in the  $P, V$  diagram [1]. We remind that *the binodal is the classical macroscopic equivalent of the modern double well or Mexican hat-type potential energy curves for the micro-world*, derived by Hund [16] to explain 19<sup>th</sup> century macroscopically observed *chiral behavior* (see also below).

The homogeneous *less ordered* gas while condensing and the homogeneous *more ordered* liquid while boiling form *a binary mixture*, with a continuously varying *molar* constitution, since the gas has different physical properties than the liquid. So, Maxwell's analysis also applies to homogeneous species and its simplest phase-transitions: changes in the state of aggregation.

*It can therefore be expected that, in nature, any possible phase-transition in a single unit of a non-composite species, by definition homogeneous, can be characterized by means of the appearance of a binodal, the shape of which is easily derived from the general shape of the Vanderwaals-Maxwell  $P, V$  diagram resulting from (4). This is the ultimate justification for the search for a universal function or UEOS. A basic difficulty is the assessment of that part of binodal and spinodal, which cannot be determined experimentally [1]. Classically, this corresponds with the existence and occurrence of negative pressures during a classical liquid-gas phase-transition, which seems like a mathematical artifact, even in the Maxwell approximation.*

The ever-continuing impact of (4), many years after its introduction and in an era full of powerful quantum and field theories, is not surprising since there is not yet a useful alternative. In addition, it is amazing that the two correction terms in (4) with  $a$  and  $b$ , are extremely simple to understand *classically*. They are directly and simply linked *to the change of model for the unit structure*, say from *point to sphere*. The term  $+a/V^2$  is a correction for *an interaction* between unit systems (neutral spheres, not points), which leads to a higher (extra internal) pressure than that applied externally (the so-called *Vanderwaals forces*). The second term  $-b$ , *a volume*, diminishes the volume  $V$  available for the system (say the vessel or the container) since the sphere-like unit structures themselves also occupy a certain volume (a self-volume). For instance, the self-volume of ideal material points, underlying the ideal gas law is zero or negligible. Its effect is that the pressure applied *externally* seems *larger* than it is, whereas the term in  $a$  makes it seem *smaller* than it is in reality.

The net effect of these two corrections shows most clearly in the corresponding  $P, V$ -diagram. Rewriting (2), we get the two opposite effects on  $P$ , since

$$P = RT/(V-b) - a/V^2 \quad (5a)$$

$$P/RT = 1/(V-b) - (a/RT)/V^2 \quad (5b)$$

Whereas the ideal gas law leads to a simple inverse power law or hyperbolic behavior of  $P$  in function of  $V$  since  $P = RT/V$ , the Vanderwaals modifications give rise to departures from this

behavior *using the simple classical arguments cited above*. The critical points, at which the inverse P, V power law is no longer obeyed, correspond with the observed phase-transitions (say liquid-gas). The shape of this observed P, V-diagram is given in Fig. 1a but it is available in any textbook on physical chemistry or thermodynamics [17]. The maximum in the P, V diagram in Fig. 1a indicated with a blackened square on the curve, arrived at when compressing the gas, plays a crucial role in the Vanderwaals-Maxwell theory (see further below). *Reversing the argument for (3) leads to the conclusion that the P, 1/V-diagram for the ideal gas must consist of (parallel) straight lines, as shown in Fig. 1b.*

INSERT Fig. 1a and 1b around here

Quantitatively, small correction terms in a and b can only have a small effect upon deviations from the ideal gas law. Only in these cases, (5a) can be expanded to give

$$P = (RT/V)(1 + b/V) - a/V^2 \quad (6)$$

Apart from one leading *linear* term in  $1/V$ , two algebraically competitive *quadratic* terms in  $\pm 1/V^2$  are generated for the deviations from the ideal gas law. These are two opposed parabolas in  $1/V^2$ , superimposed upon or instead of a straight line in  $1/V$  for the ideal gas. *In size effects of the sphere-like particle with radius r, this corresponds with variations in  $1/r^6$ .* Extracting the deviations from the ideal gas law gives

$$PV/RT = 1 + b/V - (a/RT)/V \quad (7a)$$

$$PV/RT - 1 = b/V - (a/RT)/V \quad (7b)$$

or two algebraically *competitive* linear terms in  $\pm 1/V$  for any given temperature T. *This corresponds with opposing size effects of order  $1/r^3$ .* For a and b both small, the limiting value for (7a) is 1, the ideal gas case, whereas for (7b) it is zero. The size of the vessel, determining V, must be commensurate with the physical properties of the substance –including the number of particles in the vessel– before any of the critical algebraic effects in (6) and (7), i.e. the phase transitions, can show.

Alternatively, we can compress a single particle contained in a compressor, whereby critical phenomena can only occur when the distance between piston and bottom of the pressure chamber become commensurate with the dimensions (say the diameter) of the neutral unit.

The numerical analytical difference between (6) and (7) of restrictive validity (expansion for small b) and the original versions (4) and (5) is extremely important for fitting data, as for instance done for the pseudospinodal of Boanza-type [15], as remarked in [1]. This is indicated in Fig. 1a for contribution  $1/(V-b)$  *where the power fit is clearly in error with respect to the smooth line joining the data points.* The error increases with decreasing V. A similar remark applies to contribution  $-a/V^2$ , a perfect parabola in the  $1/V$  representation, which can *never* be fitted with a power law in V due to its negative sign (this is why in Fig. 1a the term  $+a/V^2$  is shown).

To illustrate some of these difficulties, we also give Fig. 1b, which is the corresponding P,  $1/V$  diagram, with essentially the same meaning as Fig. 1a. Only variable V has been inverted to  $1/V$ . In this form the function can be fitted accurately, which is not so for the curve(s) in Fig. 1a. The ideal gas law term is now a straight line indeed, as remarked above, whereas the two Vanderwaals correction terms in (4) when added, give rise to a *binodal* or a *Mexican hat type curve*. Obviously, the function must vanish at  $1/V=0$ , since this corresponds with the absence of a particle<sup>3</sup> (zero pressure, infinite volume) in the P, V diagram. But due to its very manageable analytical behavior, we can nevertheless extrapolate the curve towards *negative*  $1/V$ , as illustrated in Fig. 1b. A slightly distorted binodal or a Mexican hat type curve emerges, which confirms our above interpretation of 19<sup>th</sup> century classical binodals. Understanding this in terms of physics may not seem straightforward but it is. When interpreted with a *density*, a *negative* volume stands for a *negative* mass particle. Hence, the 19<sup>th</sup> century Vanderwaals-Maxwell analysis allows us to extrapolate the observed behavior of neutral positive mass particles towards the hypothetical negative mass world. *We immediately verify de visu that that algebraic symmetry is broken.* In addition, we

<sup>3</sup> This corresponds with the famous sentence in Corneille's El Cid: *Et le combat cessa faute de combattants.*

observe that the well in the positive mass world originates from a *negative* pressure, one of the most difficult problems in connection with Vanderwaals-Maxwell theory and of phase-transitions in general (see the problems with pseudo-spinodals mentioned in [1]). Only to arrive at similar tangents in both worlds, we must shift the negative pressure line as shown in Fig. 1b (broken straight line). Although this may clarify some of the analyticity problems associated with binodals and spinodals for macro-systems [1], the ultimate problem is to associate all of these complicating aspects towards the unit particle, a single neutral positive mass particle like H.

*The next question is therefore what happens if we go over to a micro-system, consisting of only one neutral unit (atom) contained in a non-interacting vessel commensurate with its size. Although for ionic crystals the situation is quite clear and relatively simple as remarked above in (a), the problem is more difficult for other (non-ionic) systems like the hydrogen gas or the hydrogen atom, the system we will study below.*

As stated in the Introduction, even at the low particle level ( $X_n$ ,  $n=3,4,5$ , say  $Na_3$ ) it is necessary, to understand their internal mechanics, to invoke Mexican hat-type potentials (binodals) [3]. In small systems, similar internal phase-transitions must occur as those observed in the macroscopic world (Maxwell's binodal) and we could expect that for  $X_1, X_2 \dots X_n$  a similar situation holds, which, finally must lead to a useful analytical UEOS.

Nevertheless, in terms of scaling (scale reduction), the transition from macro- to micro-system in the case of an ideal gas goes only and simply with the dimensionless Avogadro number  $N$  (scaling by a number), *without affecting any internal physics* as in a Vanderwaals equation. We get

$$P(V/N) = kT \quad (8)$$

and can now define the critical commensurate volume  $V$  as  $N$  times the volume  $v$  of a *single* neutral particle (atom, molecule), giving  $V=Nv$ . With Boltzman's constant  $k=R/N$ , (8) becomes

$$Pv/kT = 1 \quad (9)$$

*which should be as valid for an ideal neutral unit as (1) or (5) is valid for a mole or  $N$  units, forming the ideal homogeneous gas. Pure scaling with Avogadro's number suggests that the ideal internal energy  $U$  of  $1/r$ -type is equally applicable to the micro-world.*

The next problem is then to verify experimentally how the single unit (the neutral atom) itself behaves under size variations, like expansions or compressions. If these variations obey (9), the behavior of this unit structure, the atom, can be called *ideal*. If it does not, for instance if it would obey a Vanderwaals-type equation (4)-(7), the unit does not show ideal (say *point-like*) behavior. Then, to be consistent, we must identify the phase-transition(s) for (2), eventually hidden within this unit sphere-like structure to explain the deviations from ideal (Coulomb-type) behavior, not incorporated in (9).

*Expansion and compression of atom H, viewed from its line spectrum. A critical  $n$  at  $n=\pi$ ?*

To describe the spectral behavior of species H, a number of equivalent expressions for the internal energy of this species must be compared, using appropriate conversion factors to arrive at the best possible experimental disclosure of the internal mechanics of the species. In the case of unit H, we are led to compare equivalent energy expressions like

$$Pv_H = \frac{1}{2}m_H v_H^2 = am_H c^2 = ae^2/r_H = U_H \quad (10a)$$

either with microscopic thermodynamic critical values for

$$kT \text{ or } kT_H \quad (10b)$$

as derived from (7a). If we want to use *spectral* data with electromagnetic fields, we can use similar H-specific expressions like

$$hv_H = hc/\lambda_H = (2\pi e^2/\alpha)/\lambda_H \quad (10c)$$

where we made use of Sommerfeld's fine structure constant  $\alpha$  (a field scale factor)

$$\alpha = e^2/\hbar c = 2\pi e^2/hc \quad (10d)$$

The appearance of the ratio of concurrent energy expressions  $hv_H/kT_H$ , e.g. the ratio (10c) and (10b), for the microscopic world must not come as a surprise since it is also at the roots of the Planck-Einstein equation for the specific heat of neutral particles (diatomic molecules) from which quantum theory and wave mechanics were finally derived.



If we want to be complete, we could even include gravitational effects like

$$m_H g_H \quad (10e)$$

as attempted already elsewhere [18]. These are the most likely unit energy expressions to be connected directly with mass unit H, since practically all of them, whether or not in combination, are needed to describe species H in full, both in the micro- and in the macro-world.

There are, of course, great expectations about the congruency, if not identity, between UEOS of classical Vanderwaals-type, bound to macroscopic behavior, and universal potential functions UPFs, corresponding with the description of the internal mechanics (and possible phase-transitions) within the unit structure itself (atom, molecule). For UPFs, wave (or quantum) mechanics is needed to describe its internal structure effects. *However, irrespective of any theoretical framework, accurate information on its internal mechanics is experimentally assessable with line spectra for atoms or with band spectra for molecules, due to concurrent energies of type (10).* All these contributions and efforts illustrate the importance of the transition between macroscopic and microscopic behavior in nature, as remarked in the Introduction.

To make the present discussion more transparent, we skip the effect of equating (10a) and (10c) directly, which is a problem in its own right and which is discussed in full elsewhere [19]. As shown there, equating the two leads, *from first principle's only*, quantitatively and very simply to a critical value for Bohr's principal quantum number n, equal to irrational  $\pi$  or

$$n = \pi \quad (10f)$$

*completely invisible in bound state QED* (see review [20]) as well as in original Bohr theory, for reasons explained in [19]. This identity (10f) will be referred to below in connection with the observed binodal for single neutral species H.

*Atom as a micro system. Ideal atom law. Quantitative criteria.*

To make the cases comparable, we must find an equivalent of the ideal gas law (without phase-transitions) in the macroscopic world with some law, describing the behavior of a single ideal atom (or molecule), *without a phase-transition*.

Let us therefore return to the apparent correlation between the EOS of an ionic crystal and the UPF for the single ionic bond. For ionic crystals, the Madelung form factor, as well as compressibility data suffice to arrive at a turning point in the EOS using the ionic Coulomb law. Repulsive forces of type  $+1/R^n$  ( $n \gg 1$ ) in the single ionic bond AB have a similar effect on the same Coulomb law  $-1/R$  around the equilibrium distance. According to [1], the problems to assess the analytical form of UEOS and/or UPFs are almost identical: finding the real asymptote (*the best bond energy*), which defines the final shape of the PEC or EOS (eventually containing a binodal and spinodal if there were a phase transition of any kind). If, as we proposed recently [4], the most likely UPF for molecule XY with bond length  $r_{XY}$  were an ionic Coulomb law, we get

$$U_{XY} = -ce^2/r_{XY} \quad (11)$$

The correlation with macroscopic EOS (1) is that *the internal energy* (pressure) within a single molecule increases (absolutely) with decreasing separation between its bonding partners, pending the value of c or that *U varies inversely with r*. In other terms, the U, 1/r diagram for the single bond XY should be a straight line, just like we found [4]. This behavior resembles the P, 1/V-diagram for aggregates of molecules XY (see above, paragraph (b) and Fig. 1b) since a pressure is dimensionally equivalent to an energy divided by a volume.

If there is really a correlation between (3) and (11), this can only be valid when (3) is scaled by N as in (9), which means that the aggregate of N atoms or molecules is reduced to a single atom or a single molecule. *Then the central issue is to find out what exactly are the remains of the non-covalent Vanderwaals-type forces underlying (4) within a given single structure (atom, molecule), if any.*

The molecular PECS and the possible UPF were discussed in [2,4]. As stated in the Introduction, we must now stress the similarity between the *deviations* from classical EOS (3) as conceived by Vanderwaals in his famous equation (4) for the ideal hydrogen gas and those observed for equally classical scaled EOS (9), which means a UPF for the single atom H, as indicated in (2).

Although the discussion seems to become of academic interest only, also the problem of the influence of pressure upon the internal structure of (single) atoms is of longstanding interest [21] as it could provide with a direct quantitative link between EOS (3) and UPF (5), eventually leading to a UEOS.

*We can, however, still proceed analytically to solve this intriguing matter.* Coulomb's law can only be considered as the universal law for ideal ionic molecules [4] if and only if the ionic instead of the non-ionic or covalent bond energy (asymptote) is used for scaling [2,4,8]. Then, size variations for *any Coulomb system* are generically fixed with

$$r = nr_0 \quad (12a)$$

Subsequently, we obtain formally for (1)

$$-[U(r=1.r_0) - U(r=\infty.r_0)] = -U(r_0) = e^2/r_0 \quad (12b)$$

Only by defining  $U_0$  as  $-e^2/r_0$ , we can consistently go over to a pure number theory since

$$U(r)/U(r_0) = r_0/r = 1/n \quad (12c)$$

whereby the nature of the interaction, determined by  $e^2$ , does not even interfere. The full analytical treatment for this case, even *covalent* molecule  $H_2$ , is given in [4].

In line with (12), it is simple to move to single atom like H, using Bohr theory for the ideal (circular) orbit model for *any rotator* subject to a *central Coulomb force*. We get

$$r = n^2 r_0 \quad (13a)$$

instead of linear  $n$ -dependence (12a) for the static ionic bond or for any Coulomb system.

With standard Bohr theory for the ideal rotator, we obtain energies

$$U_H = E_{nH} = -R_H/n^2 = -(1/2e^2/r_H)/n^2 \quad (13b)$$

where  $E_{nH}$  is the energy of level  $n$ ,  $R_H$  is the Bohr Rydberg,  $r_H$  is the H-radius and  $n$  is the principal quantum number.

In terms of the formulation with free energies as in (1), we arrive at the Rydberg, since

$$-[U_H(n=1) - U_H(n=\infty)] = 1/2e^2/r_H = 1/2m_H v_H^2 = R_H \quad (13c)$$

This is rather accurately known experimentally ( $109678.7737 \text{ cm}^{-1}$ , an accuracy of 3 MHz) [22]. Similarly, we can move to a pure number notation as in (12c) realizing however that we now obtain a quadratic dependence, since

$$U_H(r)/U_H(r_0) = r_0/r = 1/n^2 \quad (13d)$$

Nevertheless, spectral lines, positive term-values  $T_{nH}$ , are arrived at with a *difference* not with a *ratio*.

In fact, observed  $T_{nH}$  provide  $E_{nH}$  in Bohr theory by means of

$$T_{nH} = R_H(1-1/n^2) = R_H + E_{nH} \quad (14a)$$

leading to  $T_{1H}=0$  for  $n=1$  and to  $T_{\infty H} = R_H$  for  $n=\infty$ , the standard reference *binding energy* or *asymptote* we wish to have available in the first place, according to (1).

*As a first consequence when looking at (13b), phase-transitions within H are not allowed or are not covered by Bohr atom theory, just like the ideal gas law (point-model) as it stands cannot cope analytically with phase-transitions either. Also, a dilemma or dual interpretation emerges: if H were just a Coulomb system, its size variations  $r/r_0$  are linear in number  $n$ , see (12a) and (12c), but if it were just a true rotator like in Bohr theory, its size variations would have to go with quadratic  $n^2$  instead, see (13a) and (13d).*

### Bohr theory as an ideal atom theory, without phase-transitions (the ideal gas law paradigm)

*Near ideal behavior. Errors of Bohr theory*

Inspection of (13a) and (13b) reveals that a species like H, when being expanded as described by (13a), its internal energy varies like prescribed by (13b). The errors of Bohr theory (13b) are small, since of order  $10^{-7}$  to  $10^{-8}$  for terms if the ground state energy ( $n=1$ ) of the Bohr model is put equal to  $R_{1H} = 109678.7737 \text{ cm}^{-1}$ , the series limit given by Kelly [22] for the observed Lyman ns-series. Kelly's set contains the best set of observed data available for a near complete series of lines (Lyman ns<sup>1/2</sup>-series from  $n=1$  to  $n=20$ ) are rounded at  $0.0001 \text{ cm}^{-1}$  (or a systematic absolute error of 3 MHz).

Nevertheless, if, in reality, there were remnants of the *static* Coulomb-recipe, for which expansions should follow a linear n-dependence like in (12a), deviations must show when looking at the spectral data.

INSERT Fig. 2 around here

Fig. 2 illustrates the behavior of Bohr theory (14) in comparison with experimental data for  $T_{nH}$ , taken from Kelly [22] (see Table 1). Both sets of data are plotted versus  $1/n$ . For (14) to be valid, the fit should be perfectly quadratic for  $1/n$ , *without a linear term in  $1/n$* , as suggested by (12a). The fit<sup>4</sup> for  $T_{nH}$  shown in Fig. 2 is slightly different than predicted by Bohr's  $1/n^2$  theory

$$T_{nH} = 109678,8041 - 0.2939/n - 109678,5216/n^2 \text{ cm}^{-1} \quad (15a)$$

This result clearly indicates that *the influence of (12a), pure Coulomb scaling of type  $1/n$ , is not completely negligible and that Bohr scaling (13a) of type  $1/n^2$  is not exactly true*. Nevertheless, it seems relatively safe to conclude from fit (15a) also that the Bohr model is sufficiently accurate to serve *as an ideal atom theory*, to be understood in terms of circular orbits for the electron in the Lyman ns-series. In fact, it is not yet clear at this stage if the errors produced are of pure statistical rather than systematic/fundamental nature. To verify this, a more detailed test of Bohr theory must be provided to find out if Bohr  $1/n^2$  theory is really the measure (*the ideal atom law*). A simple way to find out if neutral species H obeys this circular model would be to compare the observed result  $T_{nH}$  (or  $-E_{nH}$ ) directly with the Bohr prediction  $R_H/n^2$  (which we will do in the Results section).

A remarkable consequence of the fact that both (12a) and (13a) may be valuable solutions for unit system H, when looking at fitted result (15a), is that their arithmetic mean

$$r/r_0 = \frac{1}{2}n(n+1) \quad (15b)$$

for  $r/r_0 = 1$  returns the quadratic relation

$$\frac{1}{2}n^2 + \frac{1}{2}n - 1 = 0 \quad (15c)$$

with solutions  $n=-2$  and  $n=1$ . Other consequences of this strange relation are given in [19] and in the references therein.

#### *Existence of an harmonic Rydberg for species H*

Alternatively, we may find out first if there are variations in the Rydberg if we use the integer n-values postulated by Bohr's quantum hypothesis. This generates running Rydbergs [10]

$$R_H(n) = -E_{nH} \cdot n^2 \quad (16)$$

The validity of Bohr theory now depends on the question whether or not  $R_H(n)$  is a constant, equal to  $109678.7737 \text{ cm}^{-1}$  in the whole range of the series from  $n=1$  to  $n=20$  available from Kelly [22]. If not, the possibility that *–within the constraints of the Bohr model–* a phase-transition in the H-species appears can theoretically not be ruled out, pending the shape of the corrected curve in function of n. This corresponds with the problem of deciding about the nature of the errors produced with Bohr theory, discussed in the foregoing paragraph.

An analysis based upon (16) reveals that  $R_H(n)$  values follow a perfect quadratic variation in function of  $1/n$  [10]. In fact, just like with (7), the ratio

$$(R_H/n^2)/(-E_{nH}) \approx 1 \quad (17)$$

should be close to the *ideal* value 1, predicted by Bohr theory. There is however only one Rydberg value, tangent to the complete series, which we called the *harmonic* Rydberg [10,19], with a value of  $109679.3589 \text{ cm}^{-1}$ .

If we want to assess the energies associated with hidden phase-transitions in the H-system, we must (a) choose a proper or the best running Rydberg  $R_H(n_x)$  at some particular  $n_x$ -value, (b) suppose this remains constant (as in Bohr theory) and (c) compute energy differences

$$\Delta_{nH} = |E_{nH}| - R_H(n_x)/n^2 \quad (18)$$

<sup>4</sup> Fits to order  $1/n^4$  are of QED-type. These are discussed elsewhere [10,19].

which is the procedure we will follow in this work. Then we have the choice between  $\Delta$ ,  $n$ - and  $\Delta$ ,  $1/n$ -diagrams. Since we found a new and *harmonic* Rydberg [10], choosing the best Rydberg  $R_{\text{H}}(n_x)$  to test Bohr theory, is not straightforward.

*Three Rydbergs (series limits) available to test Bohr theory for the occurrence of internal phase transitions in H*

(i)  $n_x=1$ . The original series limit, introduced by Bohr, applies to the ground state ( $n=1$ ) and can therefore be designated as  $R_{\text{H}}(n_x) = R_{\text{H}}(1)$  and has the value  $109678.7737 \text{ cm}^{-1}$ .

(ii)  $n_x=\infty$ . Bound state QED [20] calculates energies starting from the other end of the series at  $n=\infty$ . This Rydberg  $R_{\text{H}}(\infty)$  has the value  $109677.5704 \text{ cm}^{-1}$ , using the Kelly-data, as derived in [19]. This Rydberg is related to absolute Rydberg for an infinitely heavy baryon  $R_\infty$ , divided by the classical recoil correction  $(1+m_e/M_p)$ .

(iii)  $n_x=1/2\pi$  [10]. The third Rydberg we can use is the harmonic Rydberg, tangent to the series of running Rydbergs (11), as we showed recently [10,19]. Analytically, this would be the best Rydberg available in the context of Bohr theory (which requires a constant Rydberg for the complete series). This harmonic Rydberg  $R_{\text{Harm}}$  is found at a critical non-integer  $n=1/2\pi = 1.5727$  ([19], see also [10]). Its value is  $R_{\text{H}}(=1/2\pi) = 109679.3589 \text{ cm}^{-1}$  as shown in [19]. *We remark that this last critical and harmonic Rydberg does not play any role in bound state QED –unless indirectly- and, as such, is not tabulated by NIST although it is probably the only internal anchor available to discuss the internal mechanics of the H-species.*

For the sake of simplicity, we call the three Rydbergs respectively  $R_{\text{Bohr}}$  ( $n=1$ ),  $R_{\text{QED}}$  ( $n=\infty$ ) and  $R_{\text{Harm}}$  ( $n_x=1/2\pi$ ). Using these in (13) gives three sets of energy differences  $\Delta_{\text{Bohr}}$ ,  $\Delta_{\text{QED}}$  and  $\Delta_{\text{Harm}}$  respectively.

## Results and Discussion

With Kelly data for the Lyman ns-series [22], the results of (13) for the three different Rydbergs are given in Table 1 (columns 4, 5 and 6). The  $n$ ,  $1/n$  and  $T_{\text{nH}}$ -values are in columns 1, 2 and 3. The resulting diagrams  $\Delta$ ,  $n$  are in Fig. 3a-c; diagrams  $\Delta$ ,  $1/n$  are in Fig 4a-c.

INSERT Fig. 3a,b,c around here

$\Delta$ ,  $n$  diagrams for H (related to the P, V-diagram in Fig. 1a)

Reminding the classical Vanderwaals-Maxwell P, V-diagrams for macroscopic systems showing phase transitions as in Fig. 1a, it is remarkable that the shapes of the  $\Delta$ ,  $n$  diagrams for H in Fig. 3 are very similar. The most remarkable of the three is the curve in Fig. 3a for the Bohr set  $\Delta_{\text{Bohr}}$ . As we remarked for Fig. 1a, there is a critical maximum in the compression in the P, V diagram for macroscopic systems, as indicated in diagram 3a. *For single unit H, this maximum in Fig. 3a appears at a critical n-value between 5 and 6. This is one of the most curious and particular results of the present investigation, which needs further and thorough analytical treatment, which we will present elsewhere [24].* It is obvious moreover that this critical n-value is intimately and exclusively connected with the Bohr asymptote  $R_{\text{Bohr}}$ , since the two other asymptotes do not lead to this information (see Fig. 3).

We cannot verify at this instance whether or not Maxwell's rule, i.e. that the surfaces of the positive and negative deviations of the curve from a horizontal line in Fig. 3a, is obeyed for the isothermal expansion or compression of species H. Since this rule is so important for many other laws in thermodynamics, we must await results on the associated adiabatic process.

These 3 figures also illustrate how important it is to choose the correct asymptote to describe, eventually, in a consistent way phase-transitions [1] as we also remarked above.

Nevertheless, the inescapable conclusion from these  $\Delta$ ,  $n$  diagrams for H is that the neutral H species exhibits a phase-transition described with a curve (Fig. 3a), completely in line with the Vanderwaals-Maxwell description for macroscopic aggregates in Fig. 1a. The next

conclusion is then that species H is a binary mixture of two different states (2). How to interpret this or conversion process (2) in the microscopic world is a real challenge.

The *first* option possible is connected with the circular Bohr model, whereby total angular momentum (or any of its constituents), perpendicular to the plane of rotation, changes sign. This would lead to the classical distinction of two different spin-states for atom H: H( $\uparrow$ ) and H( $\downarrow$ ) or H(+ $\frac{1}{2}$ ) and H(- $\frac{1}{2}$ ).

Obviously, the *second* option is that in which the H-species can be present in an atom state and in a *charge-inverted* antiatom-state, which is a distinction very similar with the spin-states, since we would get H(+1) and H(-1) or *hydrogen* H and *antihydrogen*  $\bar{H}$ . Here the internal charge distribution changes from +1 (electron-proton) to -1 (positron-antiproton).

We remark that none of the three curves in Fig. 3 can be fitted with reasonable success (we tested to order  $n^6$ ). Similar fitting difficulties were already discussed when we presented Fig. 1a and Fig. 1b above. At the end, these are important for the analyticity of binodal and spinodal, the main point raised in [1]. In that context, it remains important to assess as analytically and as quantitatively as possible that part of the P, V or P, 1/V diagram for unit H in the most difficult region of interest, where we are confronted with so-called negative pressures. Exactly in this region, pseudo-spinodals have been constructed [15], which, apparently, do not obey the analyticity characteristics of a UEOS we would expect [1].

$\Delta$ , 1/n diagrams for H (related to the P, 1/V diagram in Fig. 1b). Binodal (Mexican hat curve) for species H.

INSERT Fig. 4a,b,c around here

The most remarkable difference with the  $\Delta$ , n diagrams above is that *accurate* fitting is possible in all three cases, which is an element in favor in the problem of analyticity of UEOSs [1]. The shift in the position in the extremes is due to the fact that the 3 Rydbergs are *numerically* different, which entrails varying contributions in the second order Bohr term in  $1/n^2$ .

Analytically, the global curves in Fig. 4 are of *simple* QED-type [20], i.e. with a cut off at  $1/n^4$  or

$$\Delta_x = a_x/n^2 + b/n^3 + c/n^4 \quad (19)$$

Different  $a_x$  and constant b and c will cause the extremes of (19) to shift with a different Rydberg as easily verified when looking at the three curves in Fig.4a to 4c. For derivations of (19) we get

$$d\Delta_x/dn = (d/dn)(a_x/n^2 + b/n^3 + c/n^4)$$

which produces extremes, commensurate with the critical n-value between 5 and 6 as observed in Fig. 3a in the corresponding Bohr  $\Delta$ , 1/n diagram.

In these diagrams, however, the *harmonic* Rydberg, overlooked in bound state QED, now shows its importance, as announced earlier [10]. Only the curve in Fig. 4c has a perfect Mexican hat shape, if it is extrapolated into the negative  $-1/V$  world, exactly as in Fig. 1b. This curve 4c is obviously the equivalent of the binodal in classical Vanderwaals-Maxwell theory in Fig. 1b. This confirms our conclusion above from the  $\Delta$ , n diagrams in Fig 3 that two different phases (2) occur in natural species H, when its spectrum is being measured [19].

*In addition, the maximum in the  $\Delta$ , 1/n diagram in Fig. 4c is quite exactly at  $n=\pi$ , in agreement with expectation (10f), derived using first principles only [19].*

Given the analytical form of this binodal for neutral species H and its situation on the reference frame, it is straightforward to extract the *spinodal* too, although additional problems are generated in trying to do so. These will be discussed and analyzed elsewhere, since to proceed along these lines, we must go over to *numerical* diagrams, just like in the reduced *numerical* Vanderwaals equation.

The first purpose of this work was to exhibit the beautiful harmony in the H-species, when the *harmonic* Rydberg is used to describe its internal mechanics. The importance of this harmonic Rydberg [10] was never acknowledged in bound state QED, nor by NIST, who even failed to tabulate its value [23].

Finally, the reason why the curves in Fig. 3 can not be fitted exactly is obvious when looking at the underlying analytical form (7): two inverse power laws  $1/V$  of opposite *sign* can never be fitted with linear  $V$ . This is an important aspect of the analyticity requirements for UEOS, as remarked in [1].

## Conclusion

Analyticity requirements for functions claiming UEOS status are important [1]. But it is also apparent that, as soon as there is a connection between the macro- and microscopic behavior of *neutral matter*, suggesting the existence of a UEOS, we could have concluded already a long time ago, using the observed terms of the hydrogen line spectrum, *that there must be an internal phase-transition even in the electron-proton bond*. This transition shows clearly at a critical  $n$ -value between 5 and 6, not covered by Bohr theory and not even by bound state QED. Analyzing the H-spectrum in a classical pre-quantum Vanderwaals-Maxwell-way, we find novel information, not detectable by highly sophisticated bound state QED [20]. Both this critical  $n$ -value and the usefulness of the overlooked *harmonic* Rydberg expose the existence of two different phases possible for neutral H. This is why bound state QED cannot be validated as it stands [10], especially in view of our alternative explanation for standard Lamb-shifts [10]. A next challenge is to reconcile the critical  $n$ -value between 5 and 6 in the Bohr  $\Delta, n$  diagram with the critical value  $n=\pi$  (10f), reproduced in the harmonic  $\Delta, 1/n$  diagram. This will be presented elsewhere [24].

With respect to the antihydrogen problem, we now confirm our earlier conclusion [10, 19,25] that an antihydrogen-phase is present in nature. This view runs ahead of CERN-AD-based antihydrogen experiments. We suspect that the first conclusions of ATHENA- and ATRAP-collaborations [11-13] may well be premature [19].

The search for a universal equation, which may unify both EOSs and UPFs, must go on. If the present results are confirmed, it may well turn out that there is much more similarity than hitherto believed between the analytical procedures applied in microscopic (bound state) QED, using Bohr-Einstein-Sommerfeld-Dirac-theories, and those applied in macroscopic hyperclassical 19<sup>th</sup> century Vanderwaals-Maxwell-theories. At least the detection of an internal phase-transition in natural species H as reported here, *using experimental data available for many a decade*, may lead to new insights in our understanding of the real harmony in neutral matter. A phase-transition in the Coulomb electron-proton bond must then be a very important example, if not the prototype.

## Acknowledgements

I thank M. Tomaselli and B. Sutcliffe for discussions and Y.P. Varshni for correspondence.

## References

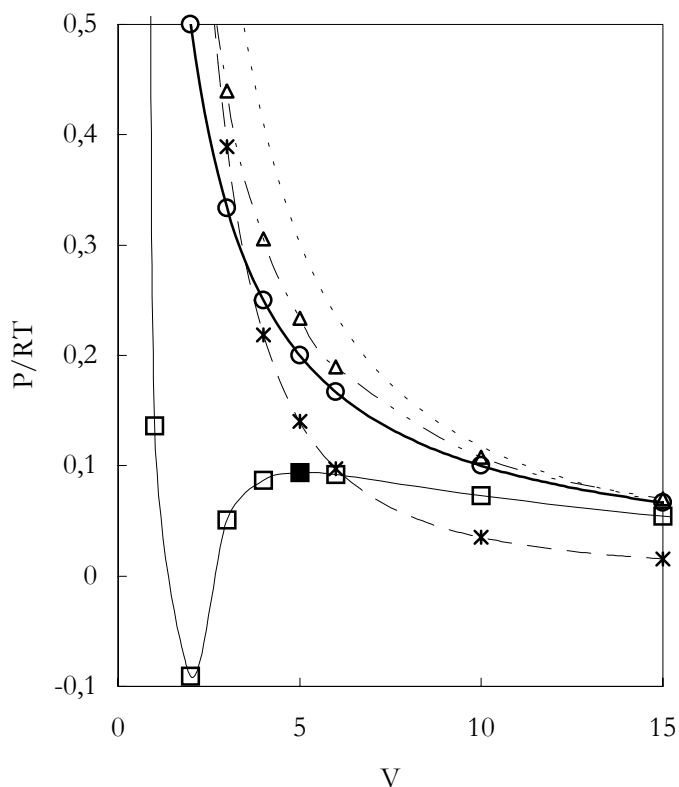
- [1] E. Brosh, G. Makov and R.Z. Shneck, J. Phys. Condens. Matter **15**, 2991 (2003)
- [2] G. Van Hooydonk, Eur. J. Inorg. Chem., 1617 (1999)
- [3] W.E. Ernst and S. Rabrovsky, Ber. Bunsenges. Phys. Chem. **99**, 441 (1995); Phys. Rev. Lett. **74**, 58 (1995)  
L. H. Coubert, W.E. Ernst and O. Golonzka, J. Chem. Phys. **117**, 7102 (2002)
- [4] G. Van Hooydonk, Spectrochim. Acta A **56**, 2273 (2000); physics/0003005
- [5] Y.P. Varshni, Rev. Mod. Phys. **29**, 664 (1957)
- [6] P. Vinet, J. Ferrante, J.R. Smith and J.H. Rose, J. Phys. C: Solid State Phys. **19**, L467 (1986)  
P. Vinet, J.R. Smith, J. Ferrante and J.H. Rose, Phys. Rev. B **35**, 1945 (1987)
- [7] J. H. Rose, J.R. Smith, F. Guinea and J. Ferrante, Phys. Rev. B **29**, 2963 (1984)
- [8] G. Van Hooydonk, Z. Naturforsch. A **37**, 710 (1982)
- [9] G. Van Hooydonk, CPS: physchem/0306001 and 0308005, submitted
- [10] G. Van Hooydonk, Phys. Rev. A **66**, 044103 (2002)
- [11] M. Amoretti et al. (ATHENA collaboration), Nature **419**, 456 (2002)
- [12] G. Gabrielse et al. (ATRAP collaboration), Phys. Rev. Lett. **89**, 213401 (2002)
- [13] G. Gabrielse et al. (ATRAP collaboration), Phys. Rev. Lett. **89**, 233401 (2002)
- [14] J. D. Vanderwaals, *Over de continuïteit van de gas- en vloeistofoestand*, Ph. D. thesis, Leiden, 1873
- [15] V.G. Boanza, M. Caceres and J. Nunez, Phys. Rev. B **28**, 28 (1995)  
V.G. Boanza, M. Taravillo, M. Caceres and J. Nunez, Phys. Rev. B **53**, 5252 (1996)

- [16] F. Hund, Z. Phys. **43**, 805 (1927)  
 [17] A. Rutgers, *Physical Chemistry*, Interscience, New York, 1954  
 [18] G. Van Hooydonk, hep-th/9902152  
 [19] G. Van Hooydonk, CPS: physchem/0302002, submitted  
 [20] M.I. Eides, H. Grotch and V.A. Shelyuto, Phys. Rep. **342**, 63 (2001); hep-ph/0002158  
 [21] Y. P. Varshni, Z. Naturforsch. A **57**, 915 (2002); J. Phys. B **30**, L589 (1997); ibidem **31**, 2849 (1998)  
 R. Dutt, A. Mukkerjee and Y.P. Varshni, Phys. Lett. A **280**, 318 (2001)  
 [22] R.L. Kelly, J. Phys. Chem. Ref. Data **16**, Suppl. 1 (1987)  
 [23] P.J. Mohr and B.N. Taylor, Rev. Mod. Phys. **72**, 351 (2000)  
 [24] G. Van Hooydonk, in preparation  
 [25] G. Van Hooydonk, submitted, CPS: physchem/0205004, <http://preprint.chemweb.com/physchem/0205004>;  
 G. Van Hooydonk, *Proceedings of the Wigner Centennial*, Pecs, 2002 (Ed. M. Koniorczyk, P. Adam)  
<http://quantum.ttk.pte.hu/~wigner/proceedings>, G. Van Hooydonk, Acta Phys. Hung., NS, Heavy Ion  
 Physics, *in the press*

Tabel 1. Quantum number  $n$  and  $1/n$ , Kelly terms  $T_{nH}$  for the H Lyman  $ns$ -series and derived energy data (all energies in  $\text{cm}^{-1}$ )

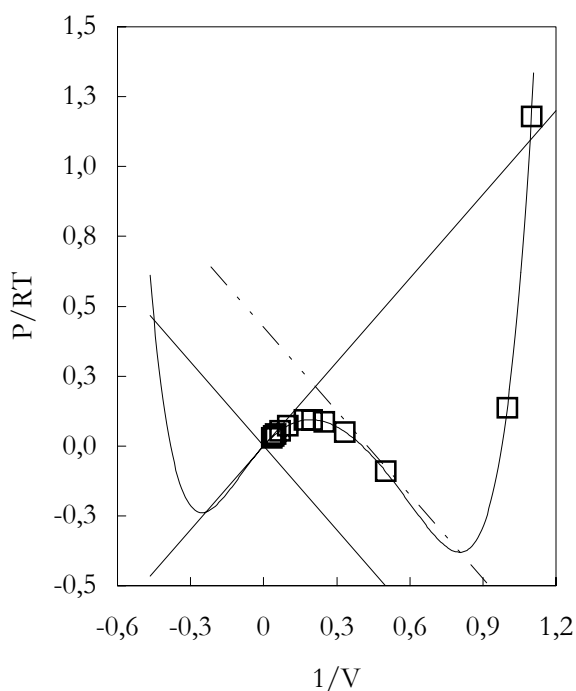
$n$	$1/n$	$T_{nH}$ (Kelly)	$\Delta_{\text{Bohr}}$	$\Delta_{\text{QED}}$	$\Delta_{\text{harm}}$
1	1,00000	0,0000	0,0000	0,0000	0,0000
2	0,50000	82258,9559	-0,1244	0,7781	-0,5633
3	0,33333	97492,2235	-0,0198	1,0498	-0,5400
4	0,25000	102823,8549	0,0046	1,1327	-0,5441
5	0,20000	105291,6329	0,0101	1,1653	-0,5516
6	0,16667	106632,1518	0,0107	1,1806	-0,5582
7	0,14286	107440,4413	0,0099	1,1887	-0,5633
8	0,12500	107965,0517	0,0088	1,1933	-0,5672
9	0,11111	108324,7225	0,0077	1,1962	-0,5702
10	0,10000	108581,9928	0,0068	1,1981	-0,5725
11	0,09091	108772,3435	0,0059	1,1993	-0,5744
12	0,08333	108917,1208	0,0053	1,2002	-0,5759
13	0,07692	109029,7916	0,0047	1,2009	-0,5770
14	0,07143	109119,1923	0,0042	1,2013	-0,5780
15	0,06667	109191,3163	0,0038	1,2018	-0,5788
16	0,06250	109250,3444	0,0034	1,2020	-0,5795
17	0,05882	109299,2655	0,0031	1,2023	-0,5800
18	0,05556	109340,2618	0,0028	1,2024	-0,5806
19	0,05263	109374,9569	0,0025	1,2025	-0,5811
20	0,05000	109404,5791	0,0023	1,2026	-0,5814

Fig. 1a. Classical Vanderwaals P, V diagram from  $P/RT = 1/(v-b) - (a/RT)/v^2$  (5a) with  $b=0,725$  and  $a/RT=3,5$ .



$P/RT$  from (5b)  $\square$ ,  $P/RT$  ideal gas law  $\circ$ ,  $+(a/RT)/v^2$   $*$ ,  $1/(v-b)$   $\Delta$ , short dashes power fit  $1/(v-b)$

Fig. 1b P, 1/V diagram: binodal (same data as in Fig. 1a)



$P/RT$  curve  $\square$ ; full straight lines crossing at origin  $+1/V$  and  $-1/V$ ; dashed straight line: shifted  $-1/V$



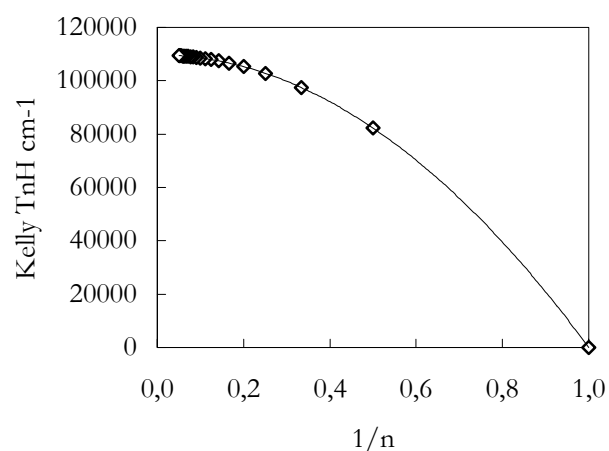
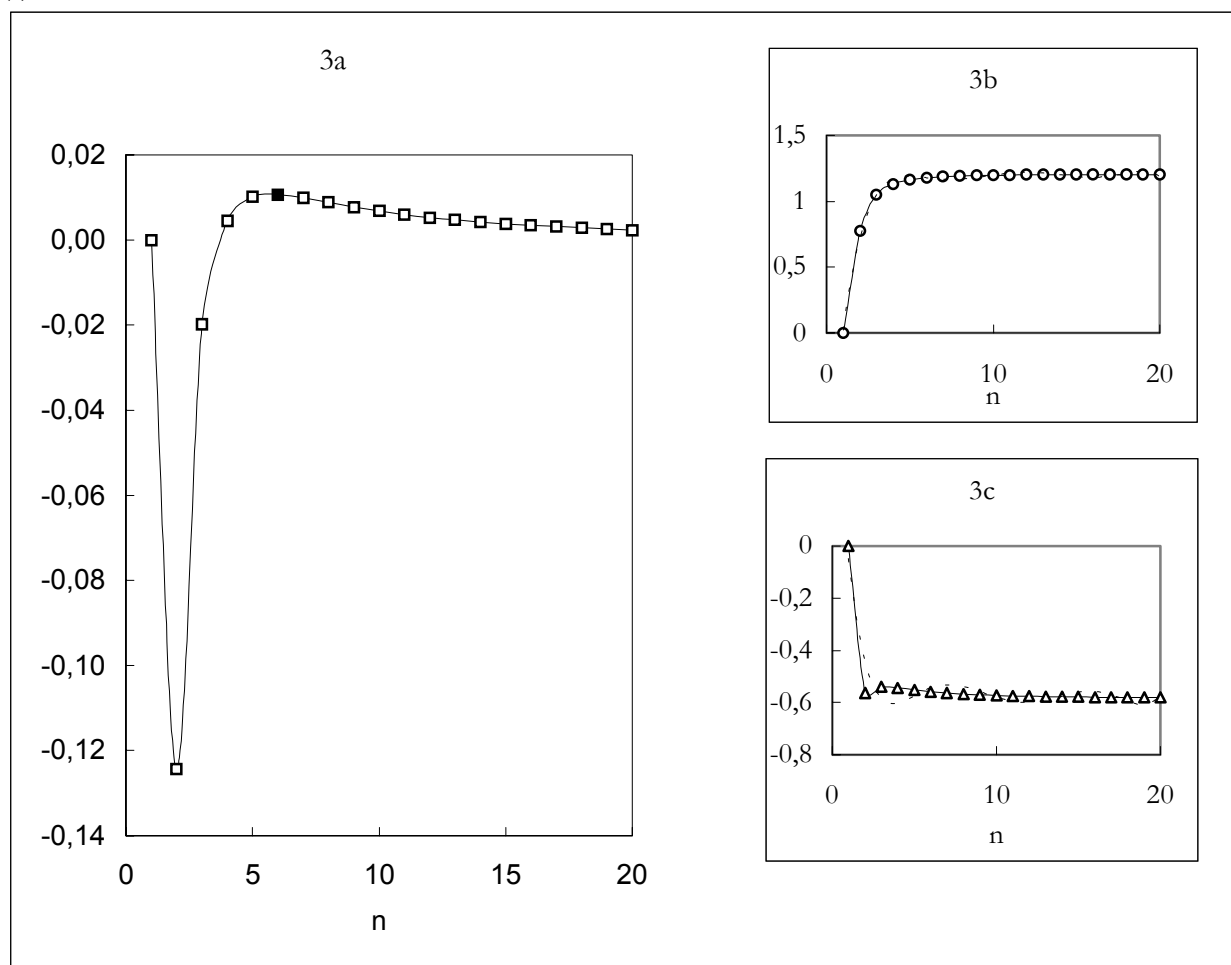
Fig. 2 Kelly terms  $T_{nH}$  for the H Lyman series versus  $1/n$ Fig. 3 a,b,c. Observed  $\Delta_{\text{Bohr}}$  vs.  $n$  (a),  $\Delta_{\text{QED}}$  vs.  $n$  (b) and  $\Delta_{\text{harm}}$  vs.  $n$  (c) diagrams for H (a)

Fig. 4 a,b,c. Observed  $\Delta_{\text{Bohr}}$  vs.  $1/n$  (a),  $\Delta_{\text{QED}}$  vs.  $1/n$  (b) and  $\Delta_{\text{harm}}$  vs.  $1/n$  (c) diagrams for H

