

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/230257697>

# ChemInform Abstract: Stability and Protonation of Multielectron Systems: The Concept of Proton Affinity. Part 1. Vague Limits

ARTICLE *in* INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY · SEPTEMBER 2012

Impact Factor: 1.43 · DOI: 10.1002/qua.22811

---

CITATIONS

4

---

READS

22

## 1 AUTHOR:



Eugene S Kryachko

University of Liège

139 PUBLICATIONS 2,026 CITATIONS

SEE PROFILE

---

# Stability and Protonation of Multielectron Systems: The Concept of Proton Affinity. I. Vague Limits

---

**EUGENE S. KRYACHKO**

*Bogolyubov Institute for Theoretical Physics, Kiev-143, 03680 Ukraine*

*Received 15 March 2010; accepted 13 April 2010*

*Published online 31 August 2010 in Wiley Online Library (wileyonlinelibrary.com).*

*DOI 10.1002/qua.22811*

---

**ABSTRACT:** The present work is a kind of a “polyphonic” collection of thoughts about the relationship between the stability of multi-electron systems and the protonation. The intricacy of the protonation sites and the protonated states that are absorbed into the concept of the proton affinity is discussed, particularly addressing its range of validity. This work can also be considered as an attempt to have a look “at different angles” at one of the most important molecular processes that occur in nature and that are reflected in our mirror of the perception of nature. ©2010 Wiley Periodicals, Inc. *Int J Quantum Chem* 111:1792–1807, 2011

**Key words:** multielectron system; protonation; proton affinity; stability; alanine

“As a grad student at Columbia around 1950, I had the rare opportunity of meeting Albert Einstein. We were instructed to sit on a bench that would intersect Einstein’s path to lunch at his Princeton home. A fellow student and I sprang up when Einstein came by, accompanied by his assistant who asked if he would like to meet some students.

‘Yah,’ the professor said and addressed my colleague, ‘Vot are you studying?’ ‘I’m doing a thesis on quantum theory.’

‘Ach!’ said Einstein, ‘A vaste of time!’ He turned to me: ‘And vot are you doing?’

I was more confident: ‘I’m studying experimentally the properties of pions.’

‘Pions, pions! Ach, vee don’t understand de electron! Vy bother mit pions? Vell, good luck boys!’”

Leon Lederman, “Life in Physics and the Crucial Sense of Wonder,”  
*CERN Courier*, September 30, 2009

*Correspondence to:* E. S. Kryachko; e-mail: eugene.kryachko@ulg.ac.be or e\_kryachko@yahoo.com

This article is dedicated to Sylvio Canuto on the occasion of his 60th birthday.

## 1. Molecular Stability $\Leftrightarrow$ Ground-State Existence $\Leftrightarrow$ Observation

The stability of finite multielectron systems, such as atoms and molecules, was always the forefront topic since the beginning of the last century that laid down the birth of quantum mechanics. Let's simply recall the Rutherford-Bohr solar system model of the atom [1, 2]<sup>1</sup> (see also [3]), the hydrogen atom H in particular. The latter is composed of a very light electron  $e^-$  with the mass  $m_e$  that carries a negative electric charge  $-1^2$  and a heavier nucleus, proton p, with the mass  $m_p$  and the mass ratio  $m_p/m_e \approx 1836.1526724718$ , which is symbolically designated as  $H^+$  (or H without  $e^-$  or ionized) and which possesses a positive charge  $Z = +1$ . I. e. simply  $H = e^- \cup H^+$ .

It is naïvely to think classical and mechanically and to naturally assume that due to their opposite electric charges that  $e^-$  and  $H^+$  bear, they attract each other Coulombically and, according to Bertrand's theorem [4], an electron revolves around the nucleus on the stable and closed, Kepler-type orbit [5, 6]. As it moves with acceleration, it emits electromagnetic radiation and thus loses energy, and has therefore to approach the nucleus as closer as possible and has finally to fall onto the nucleus, or the nuclear center,<sup>3</sup> implying that this, stable at a first glance, system must collapse. However and fortunately, an electron never did that and will never do it! The reason is rather trivial, the birth of this idea was not that simple though, a falling of an electron onto the nucleus in the hydrogen atom is strictly forbidden by quantum mechanics [8] that postulates the Rutherford-Bohr model of H "consisting of an electron revolving about a positive nucleus" ([8]) on some specific stationary orbit for the period of about 150 attoseconds<sup>4</sup> [9] and the average  $e^-$ - $H^+$  bond length of 1.000 545 6 bohr (or 0.529 455 7 Å [10]<sup>5</sup>). This orbit is characterized

by the lowest discrete energy  $E_0(H) = -0.5$  hartree,<sup>6</sup> the ground-state energy which is the same for every hydrogen atom, independently of its formation, for example on the Earth or the Moon, and which is definitely bounded from below. Equivalently, the boundedness of this orbit energy  $E_0(H)$  prevents the Coulomb collapse of the atom and therefore implies its possible observation [13].

To conclude, within quantum mechanics, atoms and molecules are stable formations of  $N$  electrons and  $M$  nuclei, carrying the nuclear charges  $\{Z_\alpha\}_{\alpha=1}^M$  and located at  $\{\mathbf{R}_\alpha\}_{\alpha=1}^M$ , that obey the Schrödinger equation, the mathematical embodiment of quantum mechanics

$$H\Psi = E\Psi. \quad (1)$$

The nonrelativistic multielectron Hamiltonian  $H$ ,<sup>7</sup> that enters Eq. (1) on the left-hand side, solely depends on the parameters of the problem, namely:  $N :=$  the total number of electrons,  $M :=$  the total number of nuclei,  $\{Z_\alpha\}_{\alpha=1}^M :=$  the nuclear charges, and the nuclear geometry  $\mathfrak{G} := \{\mathbf{R}_\alpha\}_{\alpha=1}^M \in \mathbb{R}^{3M}$ .  $M = 1$  corresponds to an atom  $\mathbf{A}$  which is neutral by definition, i.e.,  $N = Z$ , or to an ion which is charged, i.e.,  $N \neq Z$ .  $M > 1$  refers to molecule, or molecular complex, or molecular aggregate, to cluster, or to solid, the multielectron and multinuclear formation composed of atoms:  $\mathbf{M} = \mathbf{A}_1 \cup \dots \cup \mathbf{A}_M$ , linked together by so called chemical bonds<sup>8</sup>  $\Xi_{kl}(\mathbf{A}_k - \mathbf{A}_l)$  or simply  $\Xi_{kl}$ . Each bond  $\Xi_{kl}$  has its own bondlength  $R_{kl} = |\mathbf{R}_k - \mathbf{R}_l|$ . It is usually assumed that if  $\exists, \Xi_{kl}$   $R_{kl} \leq R_{vdW}(\mathbf{A}_k) + R_{vdW}(\mathbf{A}_l)$  where  $R_{vdW}(\mathbf{A}_k)$  is the van der Waals radii of  $\mathbf{A}_k$ . One then propose the working definition of the molecular structure of  $\mathbf{M}$  or, speaking rigorously, one of its isomer: the structure  $\mathfrak{Str}$  of  $\mathbf{M}$ , formally  $\mathfrak{Str}(\mathbf{M}) := \{\Xi_{kl}(\mathbf{A}_k - \mathbf{A}_l) | \forall \mathbf{A}_k, \mathbf{A}_l \in \mathbf{M}\}$ . It is natural to treat  $\mathfrak{Str}(\mathbf{M})$  as a bonding manifold.

<sup>1</sup>The term "Rutherford atom" was introduced by N. Bohr.

<sup>2</sup>In the atomic units which are largely employed throughout this entire work. One exception is Example 4 in Part II that uses  $1/4\pi\epsilon_0$ . Another is Appendix A.

<sup>3</sup>The fall of a particle onto an attractive center is also treated quantum mechanically [7]. See also Appendix A.

<sup>4</sup>The attosecond,  $10^{-18}$  s, is a quintillionth of a second.

<sup>5</sup>The average  $e^-$ - $D^+$  bond length comprises of 1.0002724 bohr (0.5293111 Å [10]) that manifests the asymmetry of the electron density near D and H and results in a small dipole moment in HD equal to 0.000345  $\pm$  0.1 a.u. ([11]).

<sup>6</sup>The computational estimation of the ground-state energy of H is  $E_0^{\text{theor}}(H) = -109678.7717 \text{ cm}^{-1}$  ( $-0.499734692$  or  $-0.4997278397$  hartree vs.  $-0.4998638152$  hartree for the deuterium atom [12]).

<sup>7</sup>For its explicit form see e.g., [14], Eqs. (2.4) – (3) and references therein.

<sup>8</sup>Pauling in his book [15] defined a bond as follows: "There is a chemical bond between two atoms or group of atoms in case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient *stability* to make it convenient for the chemist to consider it as an independent molecular species" (emphasis added by the author).

If  $M = 2$ ,  $\mathbf{M}$  is called a diatomic molecule:  $\mathbf{M} = \mathbf{A}_1 \cup \mathbf{A}_2$ , if  $M = 3$ , it is triatomic:  $\mathbf{M} = \mathbf{A}_1 \cup \mathbf{A}_2 \cup \mathbf{A}_3$ , and so on. If  $M > 1$  let define  $Z := \sum_{\alpha=1}^M Z_{\alpha}$ .  $\mathbf{M}$  is neutral if  $N = Z$ . In general  $N \neq Z$  and their difference,  $\mathbf{Z} := Z - N$ , determines a charge state: a positively charged or cationic state corresponds to  $\mathbf{Z} > 0$ , whereas the negative one or anionic to  $\mathbf{Z} < 0$ .

The eigenfunction  $\Psi_0(N, M, Z; \{Z_{\alpha}\}, \{\mathbf{R}_{\alpha}^0\})$  in Eq. (1) that corresponds to the lowest negative eigenenergy

$$E_0(N, M, Z; \{Z_{\alpha}\}, \{\mathbf{R}_{\alpha}^0\}) = \inf_{\{\mathbf{R}_{\alpha}\} \in \mathbb{R}^{3M}} E(N, M, Z; \{Z_{\alpha}\}, \{\mathbf{R}_{\alpha}\}), \quad (2)$$

bounded from below,

$$E_0(N, M, Z; \{Z_{\alpha}\}, \{\mathbf{R}_{\alpha}^0\}) \geq -\varepsilon(N, Z; \{Z_{\alpha}\}, \{\mathbf{R}_{\alpha}\}), \varepsilon > 0, \quad (3)$$

determines the bound ground state of the multielectron system under study. Hence, the ground state is the most stable and bound quantum state, the state with an infinite lifetime. Recall in this regard the Löwdin's definition of a molecule [16]: "A system of electrons and atomic nuclei is said to form a molecule if the Coulombic Hamiltonian  $\mathbf{H}'$ , with the centre of mass motion removed, has a discrete ground state energy  $E_0$ " (see also [17] and references therein).

One of the most fundamental problems of the theory of multielectron and polynuclear systems is the existence of the bound ground state which in turn is the criterion of stability. It does exist for the helium atom which, together with H is the most abundant element in the universe and ground-state energy comprises of  $E_0(\text{He}) = -2.903724$  hartrees, as was proved by Kato [18] in 1951 and for an arbitrary atom by Zhislin [19] in 1960 (see also [20]). In 1971, Hill [21] proved the stability of  $\text{H}_2^+ = \text{H}^+ \cup \text{e}^- \cup \text{H}^+$ , the simplest one-electron two-nuclear molecule or precisely molecular cation, and demonstrated that it has many bound states. Its ground-state eigenenergy  $E_0(\text{H}_2^+) = -0.6026342144949$  hartree [22], its geometry  $\mathfrak{G}(\text{H}_2^+)$  is determined by the single bond  $\Xi_{11}(\text{H}_1 - \text{H}_2)$  which the equilibrium bond length  $R_e = 1.05198 \text{ \AA}$  or  $\sim 2$  bohr.<sup>9</sup> In contrast, the hydrogen anion  $\text{H}^- = \text{H} \cup \text{e}^-$  possesses only one

<sup>9</sup>Note that  $\text{D}_2^+$  possesses "616542 times as many levels as for  $\text{H}_2^+$ " ([22b], p. 1027).

bound state  $^1\text{S}(1s^2)^{10}$  with the eigenenergy of  $E_0(\text{H}^-) = -0.527751$  hartree [24]. The next,  $\text{H}_2 = \text{H}^+ \cup \text{e}^- \cup \text{e}^- \cup \text{H}^+$  molecule is the simplest neutral molecule characterized by the ground-state eigenenergy  $E_0(\text{H}_2) = -1.174475688$  hartree [25].<sup>11</sup>

As the Rutherford-Bohr model of atom was proposed, the contextual meaning of stability underwent some changes and become broader, including particularly the following criteria [26–30]:

- i. the stability (3) against the collapse or falling electron(s) onto nucleus or nuclei. It is known as the stability of the first kind [26]:  $E_0(N, M, Z; \{Z_{\alpha}\}, \{\mathbf{R}_{\alpha}\})$  is finite for every  $\{N, Z; \{Z_{\alpha}\}, \{\mathbf{R}_{\alpha}\}\}$ .
- ii. the stability against dissociation or fragmentation [26–28]. This stability is valid for  $M > 1$  and, by definition, fragmentation of  $\mathbf{M}$  means breaking of one or more chemical bonds  $\{\Xi_{kl}(\mathbf{A}_k - \mathbf{A}_l)\}$  between the atoms which compose a given molecule  $\mathbf{M}$ . Each bond  $\Xi_{kl}(\mathbf{A}_k - \mathbf{A}_l) \in \mathbf{M}$  is characterized by the bond dissociation energy or enthalpy, BDE, that is defined as the difference in the ground-state energy of the diatom  $\mathbf{A}_k \cup \mathbf{A}_l$  between and the ground-state energies of  $\mathbf{A}_k$  and  $\mathbf{A}_l$ :  $\text{BDE}(\mathbf{A}_k - \mathbf{A}_l) := E_0(\mathbf{A}_k \cup \mathbf{A}_l) - [E_0(\mathbf{A}_k) + E_0(\mathbf{A}_l)]$ .<sup>12</sup> According to the Lieb-Thirring "binding criterion" [29], a many-body system  $\mathbf{M}$  is stable if  $\exists$  at least one configuration which energy is strictly less than the sum of the energies of the composing subsystems (clusters)  $\mathbf{M}_1, \mathbf{M}_2, \dots, \mathbf{M}_K \subseteq \mathbf{M}$  at infinity. This difference in energy,

$$\left[ \sum_{i=1}^K E(\mathbf{M}_i) - E(\mathbf{M}) \right] + \left[ \sum_{i=1}^K \text{ZPE}(\mathbf{M}_i) - \text{ZPE}(\mathbf{M}) \right], \quad (4)$$

<sup>10</sup> $\text{H}^-$  is present in huge amounts in the chromosphere of the Sun [23].

<sup>11</sup>In the work [25c], W. Heitler and F. London explained for the first time the H-H bonding in  $\text{H}_2$  quantum mechanically: an electron migrates between the two protons and a strong bonding force emerges as a quantum mechanical effect. Later, in 1932, Heisenberg applied this molecular binding idea to the nuclear force.

<sup>12</sup>It is clear that the BDEs of any polyatomic molecule include many-body effects and is applicable only to atoms at the exterior of a given molecule.

is defined as a so called binding energy  $E_{\text{bind}}[\mathbf{M}|\mathbf{M}_1, \mathbf{M}_2, \dots, \mathbf{M}_K]$  w.r.t. such system's decomposition. In (4) the abbreviation ZPE stands for the zero-point energy.<sup>13</sup> Speaking rigorously, the criterion (ii) is absolutely equivalent to (i), the existence of a ground state (3), if it holds for all nontrivial system's decompositions (see also [14a]). In the other words, a positivity of (4) is equivalent to the statement that  $\mathbf{M}_1, \mathbf{M}_2, \dots, \mathbf{M}_K$  are bonded<sup>14</sup> via some chemical bonds  $\{\Xi_{kl}(\mathbf{A}_k - \mathbf{A}_l)\}$  within  $\mathbf{M}$ . The Hunziker-van Winter-Zhislin theorem [19, 31, 32] (see also [33–35]) provides the variational criterion of (3) (see also [36–38] for current works).

- iii. The stability of the second kind [26] (see also [27, 28]):  $\exists$  a nonnegative function  $A(Z)$  such that for all  $N$  and  $M$ , there obeys a linear law

$$E_0(N, M, Z; \{Z_\alpha\}, \{\mathbf{R}_\alpha\}) \geq -A(Z)(N + M). \quad (5)$$

According to [30c], (5) can be particularly rewritten for atoms  $\mathbf{A} > \text{H}$  and atomic ions  $\mathbf{A}^Z$  as

$$E_0(N, Z) \geq -B(N + Z - 1) \quad (5')$$

where  $0 < B < |E_0(\text{H})| = 0.5$  (in hartree). (5') straightforwardly yields that

$$E_0(\text{H}_2^+) = -0.602634 \geq -2B, E_0(\text{H}^-) \geq -2B, E_0(\text{H}_2) \geq -3B, E_0(\text{H}_3^+) \geq -3B. \quad (5'')$$

Substituting the corresponding ground-state energies into the first three inequalities, one obtains a better lower boundary for  $B \geq 0.39149$  and thus narrows the above range of  $B$ .

- iv. The thermodynamical stability: the enthalpy or the electronic energy of a given multielectron state to a reference (asymptotic)

tote) state that can also be a cluster decomposition state.

- v. The conformational stability or thermodynamic stability of a conformer, see below.  
vi. The kinetic stability is actually a “resistance” to change that is predetermined by a rate of a given chemical reaction: the slow the reaction, the more stable the molecule.  
vii. The electronic stability is determined by the HOMO (highest occupied molecular orbital)–LUMO (lowest unoccupied molecular orbital) gap  $\Delta$ . It in fact serves as the criterion for the kinetic stability of isomers: as widely accepted [39],  $\Delta > 1.3$  eV indicates a high stability while  $\Delta < 1.3$  eV a low one.

The stabilities (i), (ii), and (iv)–(vi) are actually determined by the landscape of the 3M-dimensional<sup>15</sup> potential energy surface (PES) or hypersurface of a given multielectron system treated within the Born-Oppenheimer approximation (see [40, 41] and also [14, 17] and references therein). Each electronic state of any molecule has its own PES  $\subseteq \mathfrak{R}^{3M}$ . Each local minimum, including the global one, on a PES determines a conformer or structural isomer. Manifold of all conformers of  $\mathbf{M}$  or conformational manifold  $\mathfrak{M}(\mathbf{M})$  hence induces the energetic landscape on its PES. Each conformer  $\mathbf{M}_i \in \mathfrak{M}(\mathbf{M})$  features its own bonding manifold  $\mathfrak{Str}(\mathbf{M}_i)$ . If a multidimensional PES possesses few local minima which are separated by large barriers determined by transition structures, particularly between the local minimum and the global one (or the global ones in a degenerate case), it is unlikely, without interacting with an “environmental bath,” that a given molecular system, as being eventually localized in the local minimum, easily finds its descendent path from the local to the global one and it therefore resides for sufficiently long time in the local. Then the term “state” generally means a temporally stable or metastable “state” in which the studied system may exist for the time interval long enough to be observed with clear signatures of the identity of this conformer  $\mathbf{M}_i$ . In general, low-energy molecular isomers are hard to identify experimentally, though the experimental identifications of some low-energy isomers are reported for glycine [42a], 3-aminophenol ( $\text{C}_6\text{H}_7\text{NO}$ ) [42b], fullerene [42c],

<sup>13</sup>To have a “feeling” of the ZPE magnitude, note that, for example, the ZPE of the ground state of  $\text{H}_2^+$  comprises of 0.0102 hartree or 6.4006 kcal mol<sup>−1</sup> [22c].

<sup>14</sup>Some geometrical criteria could be quite useful here. For example, the criterion of contact or closeness of each pair of clusters to each other within the sum of the corresponding van der Waals radii.

<sup>15</sup>Unless the center of mass is removed.



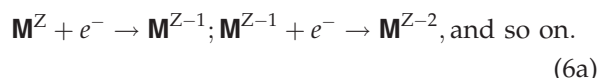
and gold clusters [42d-f]. Below, some examples which discuss relationship between the concept of molecular stability and the concept of the PES landscape are given.

## 2. Molecular Stability $\Leftrightarrow$ Charge State

In quantum chemistry, that is a part of quantum mechanics dealing with molecular or chemical species, including atoms, the traditional perception of stability largely relies on (ii) and (iv)–(vii), which are diversified by mapping onto a set of charge state(s)  $\mathbf{Z} = \mathbf{Z} - N$ , though it is still wider.<sup>16</sup> For a multielectron system  $\mathbf{M}^{\mathbf{Z}}$ , given in the charge state  $\mathbf{Z}$  with the geometry  $\mathfrak{S}_{\mathbf{M}}^{\mathbf{Z}} \in \mathbb{R}^{3M}$  and characterized by the electronic energy  $E(\mathbf{M}^{\mathbf{Z}}|\mathfrak{S}_{\mathbf{M}}^{\mathbf{Z}})$ , such charge-state mappings are realized via the following processes:

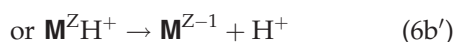
$$\bullet \mathbf{Z} \Rightarrow \mathbf{Z} - 1 -$$

Electron attachment:



that, according to the IUPAC “Gold Book” [44], is defined as the “transfer of an electron to a molecular entity, resulting in a molecular entity of (algebraically) increased negative charge. It is not an attachment.”

Deprotonation—Removal of a proton  $\text{H}^+$ :

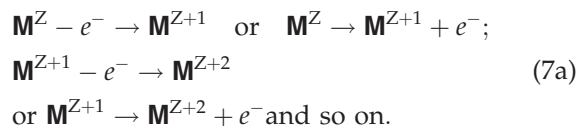


where in particular  $\mathbf{Z} = -1$  and hence  $\mathbf{M}^{-1}\text{H}^+ = \mathbf{MH}$ . It is usually suggested that deprotonation takes place with the neutral complex  $\mathbf{MH}$  that contains H. Deprotonation energy (enthalpy), DPE, is defined as

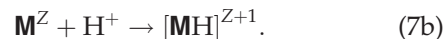
$$\begin{aligned} \text{DPE}(\mathbf{M}^{\mathbf{Z}}\text{H}) &:= [E(\mathbf{M}^{\mathbf{Z}}\text{H}) - E(\mathbf{M}^{\mathbf{Z}-1})] \\ &+ [\text{ZPE}(\mathbf{M}^{\mathbf{Z}}\text{H}) - \text{ZPE}(\mathbf{M}^{\mathbf{Z}-1})] + 5RT/2. \quad (6c) \\ \bullet \bullet \mathbf{Z} &\Rightarrow \mathbf{Z} + 1 - \end{aligned}$$

<sup>16</sup>It is a sort of chemical or reactive stability that particularly covers carbenes which microsecond lifetime is too short to study [43].

Ionization—an electron removal or loss of an electron, or whole attachment:



Protonation or proton attachment—Addition of proton  $\text{H}^+$ :



Proton affinity, PA, is defined as

$$\begin{aligned} \text{PA}(\mathbf{M}^{\mathbf{Z}}) &:= [E(\mathbf{M}^{\mathbf{Z}}) - E([\mathbf{MH}]^{\mathbf{Z}+1})] \\ &+ [\text{ZPE}(\mathbf{M}^{\mathbf{Z}}) - \text{ZPE}([\mathbf{MH}]^{\mathbf{Z}+1}) + 5RT/2]. \quad (7c) \end{aligned}$$

**Comment 1:** It does not mean at all that the molecular structure  $\mathfrak{Str}$  of the system with such  $\mathbf{Z}$  and  $N$  is a substructure of  $\mathfrak{Str}$  of that with  $\mathbf{Z} + 1$  and  $N$ , i.e., the molecular graph (see e.g., [17c] and references therein) of  $\mathbf{Z}$  and  $N$  is embedded into that of  $\mathbf{Z} + 1$  and  $N$ .

Except the most trivial system of the hydrogen atom, the rest of multielectron systems that quantum chemistry deals with are definitely many-body. Hence, these quantum mechanical problems are not exactly solvable. That is why a variety of approximate pictures that are mainly governed by variational manifolds of trial multielectron wave functions within the concept of self-consistent field (SCF), e.g., the Hartree-Fock (HF) formalism based on the Slater determinants,<sup>17</sup> the valence bond (VB) theory, different many-body perturbative methods, which are mainly based on the Rayleigh-Schrödinger and Brillouin-Wigner approaches, particularly the most exploited the second-order perturbative Møller-Plesset (MP2) formalism, various configuration interactions’ (CI) approaches, including the multireference one, a variety of coupled-cluster theories and the density functional theory (DFT), which are endowed by the Roothaan-linear-combination-of-atomic-orbitals (LCAO) structure [46, 11] to solve Eq. (1) as accurately as possible are evoked and for this reason the stability—not the physical one, the

<sup>17</sup>Note that  $\text{H}^-$  is unstable within the Hartree-Fock approach (see e.g., [14], Table IV.11). The ground-state energy  $E_0^{\text{HF}}(\text{H}_2)$  in the Hartree-Fock limit is equal to  $-1.133\,629\,571\,7(2)$  hartree [45] that lies higher the exact  $E_0(\text{H}_2)$  by  $25.631\,305\,581$  kcal mol<sup>-1</sup>.

approximate instead—naturally depends on the chosen approximate model picture. Below we present some list of the proved statements regarding this approximate stability, mostly the HF one:

**Proposition 1** (Theorems 2.1 and 2.4 [47a], Theorem [48], see also Theorem 3.2 [49]):

- i. “Assume  $Z \geq N$ , then there exists” the HF ground eigenstate (p. 36 [48]);
- ii. The stability (ii) holds for the HF multielectron eigenstate. I. e. equivalently:  $\exists$  the well-defined<sup>18</sup> HF ground-state Slater determinant  $\Psi_0^{\text{HF}}(N, M, Z; \{Z_\alpha\}, \{\mathbf{R}_\alpha^e\})$  “as soon as” (p. 300 [49])  $Z > N - 1$  that is equivalent to

$$Z \geq N. \quad (8)$$

**Corollary 1:** Note that  $\text{H}^-$  does not satisfy the inequality (17) (see also the footnote “17”).

**Corollary 2:** If a given multielectron system with  $Z$  and  $N$  that satisfy (8) is the Hartree-Fock stable, then its “analogue” with  $Z + 1 \geq N$  might be also stable as well as that with  $Z + k \geq N$  for any  $k \in N$ , where  $N$  is the set of natural numbers. Equivalently, if a given multielectron system with  $Z$  and  $N$  such  $Z \geq N$  is stable within the Hartree-Fock picture, then that with  $Z \geq N - k$  for any  $k \in N$  is likely also stable. In the other words, the ionization (7a) or protonation (7b) should not probably break the Hartree-Fock stability.

**Comment 2:** Corollary 1 implies that if the neutral multielectron system with  $Z = N$  is stable within the Hartree-Fock approach, an arbitrary multi-ionization may also yield the HF-stable system. In the other words, any multipositively charged multielectron system  $Z > N - k$  where  $k = 1, 2, \dots, N$  has likely the HF ground eigenstate. Obviously, the latter statement is not generally valid. For instance, it is evident that the system with  $Z > 0$  and  $N = 0$  is unstable. Obviously, within the HF picture, there  $\exists$  the threshold value  $N_{\text{cr}} \leq Z$  of  $N \leq Z$  as a function of  $Z$ ,  $\{Z_\alpha\}$ , and  $M > 1$ , such that the multielectron system is stable with  $N_{\text{cr}}$  and unstable with  $N_{\text{cr}} - 1$ . And inversely, for  $N$  and  $M > 1$  there  $\exists$  such critical value  $Z_{\text{cr}} \geq N$  of  $Z \geq N$  that  $Z_{\text{cr}}$  corresponds to the stable system, whereas  $Z_{\text{cr}} + 1$  yields instability. The argument is

<sup>18</sup>A well definiteness (nicety) means that a trial  $\Psi$  satisfies all necessary mathematical conditions to describe a bound multielectron state (for details see e.g., [19] and references therein).

trivial: a simple positively or negatively charged Coulomb explosion and the oppositely charged subsystem to screen the Coulomb repulsive barrier.

**Comment 3:** Except only few cases which are considered in Part II, the molecular stability has not been associated with alternating the charge of the nuclear subsystem, i.e., by adding or removing one, two or more protons  $\text{H}^+$ . Though, those cases are also natural to study. Corollary 1 implies that if the neutral multielectron system with  $Z = N$  is stable within the Hartree-Fock approach, all multiprotonated molecular species are likely also HF-stable. This statement is not generally valid since, obviously,  $\exists$  a threshold  $kP_{\text{thr}} \geq 1$  such that the  $kP_{\text{thr}}$ -protonated  $N$ -electron system with the total charge  $Z = +kP_{\text{thr}}$  fragments due to the repulsive Coulomb interaction.

### 3. Protonation and the Concept of Proton Affinity

The protonation, defined in (16b) viz.:  $\mathbf{B}(\text{g}) + \text{H}^+(\text{g}) \rightarrow \mathbf{BH}^+(\text{g})$ , where  $\text{g}$  indicates the gas phase and  $\mathbf{M} = \mathbf{B}$  is a base under study, is the fundamental phenomenon that definitely plays a central role in chemistry and biology. Its measure, the proton affinity or PA for short, is defined as the negative of the energy or enthalpy of the protonation (see e.g., [50] and references therein):

$$\text{PA}(\mathbf{B}_\alpha) := [E(\mathbf{B}) - E(\mathbf{BH}_\alpha^+)] + [\text{ZPE}(\mathbf{B}) - \text{ZPE}(\mathbf{BH}_\alpha^+)] \quad (9)$$

where  $\mathbf{BH}_\alpha^+$  is its protonated form at the neutral base site  $\alpha$ ,  $\text{ME}(\mathbf{M})$  and  $\text{ZPE}(\mathbf{M})$  are correspondingly the electronic and zero-point energies of  $\mathbf{M} = \mathbf{B}$  and  $\mathbf{BH}_\alpha^+$ . Precisely,  $\text{PA}(\mathbf{B}_\alpha)$  defined in (9) is the electronic part,  $\text{PA}_{\text{el}}(\mathbf{B}_\alpha)$ , of the total proton affinity PA which also includes, as demonstrated in Eq. (7c), the changes in the vibrational, translational, and rotational energies, and in the PV term.

**Proposition 2:**  $\text{PA}(\mathbf{B})$  is strictly positive for neutral bases.

**Proof:** It is trivial to prove this proposition. Otherwise, since  $E(\mathbf{BH}^+) \geq E(\mathbf{B}) + E(\text{H}^+) = E(\mathbf{B})$ ,  $\mathbf{BH}^+$  becomes unstable, according to (ii). Q. E. D.

**Comment 4:** If  $\mathbf{M}$  is a positively charge multielectron system,  $\text{PA}(\mathbf{M})$  can admit both signs. See, for example, Example 1 and Part II.

Equation (9) fully coincides with Eq. (4) if  $\mathbf{M} = \mathbf{BH}_\alpha^+$ ,  $\mathbf{M}_1 = \mathbf{B}$  and  $\mathbf{M}_2 = \mathbf{H}^+$ , that implies that  $\mathbf{B}$  forms with proton the bond  $\mathbf{B}_\alpha\text{-H}^+$  at the  $\alpha$ th site of  $\mathbf{B}$  and  $\text{PA}(\mathbf{B}_\alpha) = -\text{BDE}(\mathbf{B}\text{-H}_\alpha^+)$ . Mathematically, as trivially follows from (7b), protonation can be considered as the mapping  $\mathfrak{P} : \mathbf{Z} = 0 \Rightarrow \mathbf{Z} = +1$  of the manifold of bound states of  $\mathbf{M}$  in the neutral charge state onto the manifold of the bound states of  $\mathbf{MH}$  in the cationic charge state.

#### 4. Molecular Stability $\Leftrightarrow$ Protonation

In general, a molecule  $\mathbf{M}$  possesses not only a single site for protonation of a neutral base. A site of protonation is defined as an atom  $\mathbf{A}_k \in \mathbf{M}$  such that  $\text{PA}(\mathbf{M}_k) > 0$ . Depending on the topology of the PES of  $\mathbf{M}$ , on the experimental setup, and considerably on a molecular size, many possible protonation sites can be realized in experiments, not only the most energetically favorable one.

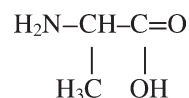
The protonation at  $\mathbf{A}_k \in \mathbf{M}$  probes and measures, in some sense, a set of chemical bonds  $\{\Xi_{kl}\}$  adjacent to  $\mathbf{A}_k$ . Exactly speaking, their strengths or their BDEs are probed by means of the intermolecular interaction between  $\mathbf{M}$  and  $\mathbf{H}^+$ . The latter is a rather strong interaction since any  $\text{PA} > \text{PA}(\text{He}) = 42.5 \text{ kcal mol}^{-1}$  (see Part II) that may obviously activate the bond at which  $\mathbf{H}^+$  resides or even causes a bond softening, or may even induce its rupture.

**Proposition 3:** Speaking rigorously, Eqs. (7b) and (9) implicitly assume that the bond pattern's manifold  $\mathbf{Str}(\mathbf{M})$  of  $\mathbf{M}$  is not broken under protonation. Therefore, its molecular structure remains unchanged, that is,

$$\mathbf{Str}(\mathbf{M}) \subseteq \mathbf{Str}(\mathfrak{P}(\mathbf{M})). \quad (10)$$

**Proof:** It is trivial. Consider Eq. (9). To prove the above statement, it suffices to suggest the contrary. Then  $E(\mathbf{B})$  in Eq. (9) should refer to another  $\mathbf{B}$ , say, to  $\mathbf{B}' \neq \mathbf{B}$ . Q. E. D.

Let us now suggest that the experimental setup is prepared in such a way that for a given molecule  $\mathbf{M}$  some its conformers  $\{\mathbf{M}_i | \mathbf{M}_i \in \mathfrak{M}(\mathbf{M})\}$  including the ground-state one  $\mathbf{M}_0$  (if it is not degenerate) that have sufficient lifetimes, are prepared to be protonated. In fact, the protonation maps  $\mathfrak{M}(\mathbf{M})$  onto  $\mathfrak{M}(\mathfrak{P}(\mathbf{M}))$ . Usually, the mapping  $\mathfrak{P}$  is "less many" to "more many." To demonstrate this, choose  $\mathbf{M}$  as  $\alpha$ -alanine

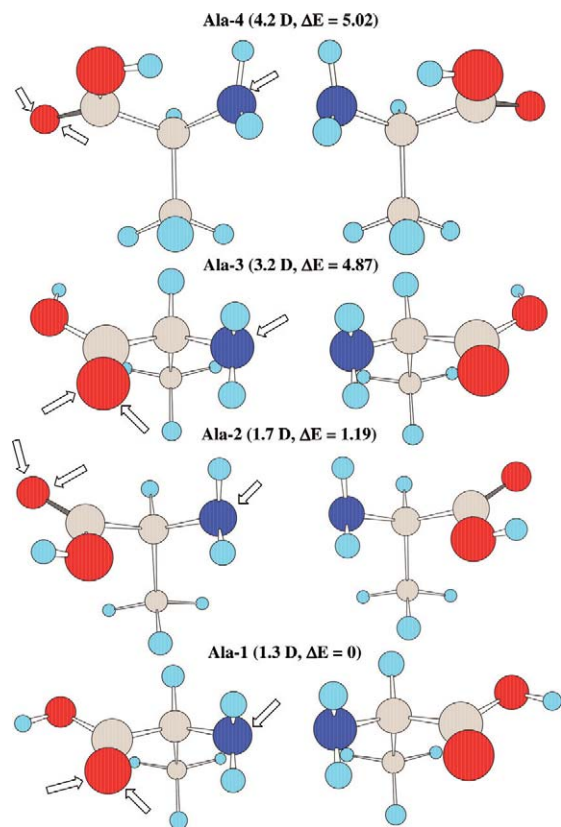


or alanine for short, throughout this work. Recall in this regard that protonation is an ordinary process of functioning of biomolecules, such as, for instance, peptides. Peptides, which acid-base properties are controlled by their amino acid constituents, can be cleaved under protonation (see e.g., [51] and references therein).

**Example 1:** Eight alanine isomers, including the most stable one **Ala-1**, are demonstrated in Figure 1 (see [52] and references therein). They are distinguished by their C—C—N skeleton and gathered into pairs with a mirror symmetry, viz., respectively, **Ala-n** and **Ala-n\***,  $n = 1 - 4$ . It is shown therein that each isomer of alanine has three sites of protonation two of which are located on the C=O group and one on  $\text{NH}_2$ . That is, formally, the mapping  $\mathfrak{P}$  is 1-to-3. Two most stable protonated isomers of alanine which possess the  $\text{NH}_3^+$  group are gathered in Figure 2. Among them, the most stable one,  $[\text{AlaH}]_1^+$ , with the lowest energy is that is resulted from mapping  $\mathfrak{P}$  of **Ala-1**, that is  $\mathfrak{P}(\text{Ala-1}) = [\text{Ala-1H}]^+$ . It is evident from Figure 2 that  $\mathfrak{P}$  does not change the bond manifold  $\mathbf{Str}(\text{Ala-1})$ . Hence, according to Proposition 3,  $\text{PA}(\text{Ala-1})$  is meaningful and is estimated equal to  $214.7 \text{ kcal mol}^{-1}$  that fairly correlates with the experimental value of  $215.7 \text{ kcal mol}^{-1}$  [50c].

Multiprotonation that does lead to fragmentation may also yield the absolutely stable molecular species, not only kinetically stable. In the other words, multiprotonation may lower the energy and thus ensures the positive second and possibly other proton affinities. The molecule of alanine is a remarkable example of the positivity of its second  $\text{PA}_2(\text{Ala}) \equiv \text{PA}_2(\text{Ala-1})$ . Figure 3 lists the three stable isomers of  $[\text{AlaH}_2]^{+2}$ . The lowest energy one,  $[\text{AlaH}_2]_1^{+2}$ , distances from the energetically closest one,  $[\text{AlaH}_2]_2^{+2}$ , by only  $\Delta E_{12}([\text{AlaH}_2]^{+2}) = 0.3 \text{ kcal mol}^{-1}$ . This difference in energy is very small, nevertheless it is distinct from zero, suggesting that the invoked computational level correctly reflects the real stability order, and these two isomers are separated by the barrier of the hindered OH rotation which is displayed in Figure 4 and amounts to  $10.1 \text{ kcal mol}^{-1}$ . The remarkable feature of diprotonated alanine is that the ground-state isomer  $[\text{AlaH}_2]_1^{+2}$ , is





**FIGURE 1.** Some isomers of alanine together with their mirror structures indicated by asterisk. Their B3LYP/6-311++G(3df,3pd)<sup>19</sup> order of relative stability in the gas phase is given by the ZPE-corrected energy difference  $\Delta E$  (in kcal·mol<sup>-1</sup>) w.r.t. the ground-state isomer **Ala-1** with the total dipole moment of 1.3 D (the isomer **1** in [52a] and **I** in [52b], both obtained at the B3LYP/6-311++G(d,p) computational level; **Ala-1\*** corresponds to the isomer **4b** in [53a] and **I** in [52c], and absent in [52b]). The next isomer, **Ala-2**, lies rather close to **Ala-1**. **Ala-2** is **3b** in [53a], which is not identified in this work, and **III** in [52b] with  $\Delta E = 1.07$  kcal mol<sup>-1</sup>, and **IIIb** in [52c]. The next two are also very close in energy to each other. **Ala-3** is **6** in [52a] and **VI** in [52b], both with  $\Delta E = 5.72$  kcal mol<sup>-1</sup>, **Ala-3\*** and **Ala-4** are absent in [52a-b], **Ala-4\*** is **7** in [52a] which is not found therein. Interestingly, the less stable isomer is the more polar. The zwitterionic form is unstable in the gas phase (see e.g., [52a]). Arrows designate possible protonation sites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

not in fact that is resulted from the ground-state alanine isomer under diprotonation, i.e.,  $\mathfrak{P}^2(\text{Ala-1}) = \mathfrak{P}(\mathfrak{P}(\text{Ala-1})) \equiv [\text{AlaH}_2]_2^{+2} \neq [\text{AlaH}_2]_1^{+2}$ .

<sup>19</sup>The computational methodology of the present work is briefly outlined in Appendix B.

Formally speaking, it implies that the second proton affinity of alanine  $\text{PA}_2(\text{Ala})$  is meaningless and thus, it cannot be experimentally measured. Well, something, that approximates  $\text{PA}_2(\text{Ala})$ , can be in principle measurable, but not correctly assigned. Nevertheless, we provide the value of  $\text{PA}_2(\text{Ala})$  as the energy difference between the ground states of the  $\text{PES}([\text{AlaH}]_1^+)$  and  $\text{PES}([\text{AlaH}_2]_1^{+2})$  – it is equal to 83.6 kcal mol<sup>-1</sup> and positive in particular.

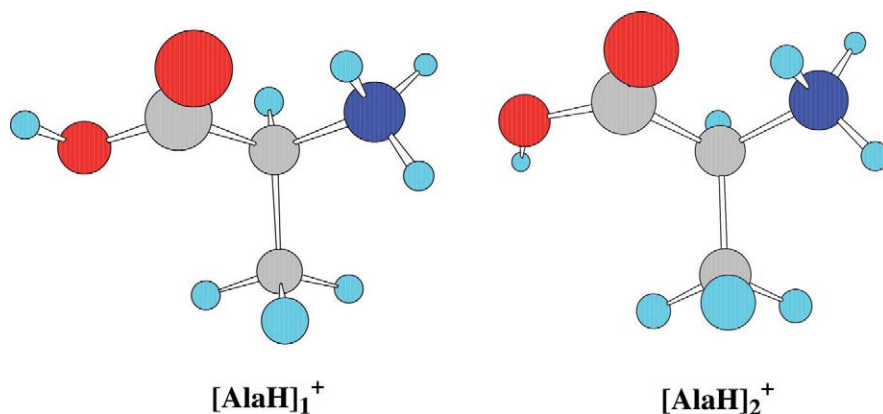
Therefore, to conclude, there may in principle exist two possible scenarios of protonation of **M**. One of them, let name it as the scenario “S” from a word “stable,” when the bonding manifold of **M** is not changed under protonation and Proposition 3 takes place. If it undergoes some changes, this refers to the scenario “U” – “unstable.” Deprotonation (6b) is one of hallmarks that distinguish these two scenarios. Deprotonation actually represents the mapping  $\mathfrak{D} : \mathbf{Z} = +1 \Rightarrow \mathbf{Z} = 0$ . Consider a multinuclear molecule **M** which possesses  $\Lambda$  sites of protonation  $\alpha = 1, 2, \dots, \Lambda > 2$ . Within the scenario “S,” a protonated conformer  $\text{MH}_\alpha^+$  is transformed under a selective deprotonation at the site  $\alpha$  exactly to **M**. In this sense, the product of deprotonation and protonation mappings,

$$\mathfrak{D}_\alpha \cdot \mathfrak{P}_\alpha = \text{I}, \quad (11)$$

is a unit operator on the bonding manifold. To some extent, this means so called deprotonation–protonation reversibility (see e.g., [54] and references therein). Because of this reversibility, the PA can be defined as the energy or enthalpy of the reaction (6b') [55].

Within the scenario “U,” each  $\mathfrak{P}_\alpha \mathbf{M} = \text{MH}_\alpha^+$  can be mapped under deprotonation into  $\mathfrak{D}_\alpha(\text{MH}_\alpha^+) := \mathbf{M}_\alpha$ , a conformer of **M**, which can be in general different from **M**. Recall here Example 1 where  $\mathfrak{D}([\text{AlaH}_2]_1^{+2}) \neq ([\text{AlaH}]_1^+) = \mathfrak{P}(\text{Ala-1})$ . This therefore implies that if the scenario “U” takes place, the definition (9) of PA is invalid and any interpretation of the experimentally measured PAs as the proton affinity of **M** is meaningless. Moreover, it may happen within this scenario that one or more of these  $\mathbf{M}_\alpha$  may be located energetically below **M**, that is, they are more stable compared to **M**. We thus arrive at the following:

**Proposition 4:** If  $\mathfrak{Str}(\mathbf{M}) \not\subset \mathfrak{Str}(\mathfrak{P}(\mathbf{M}))$ , that takes place for dissociative protonation, the PA loses its meaning and the concept of the proton affinity is no longer valid.

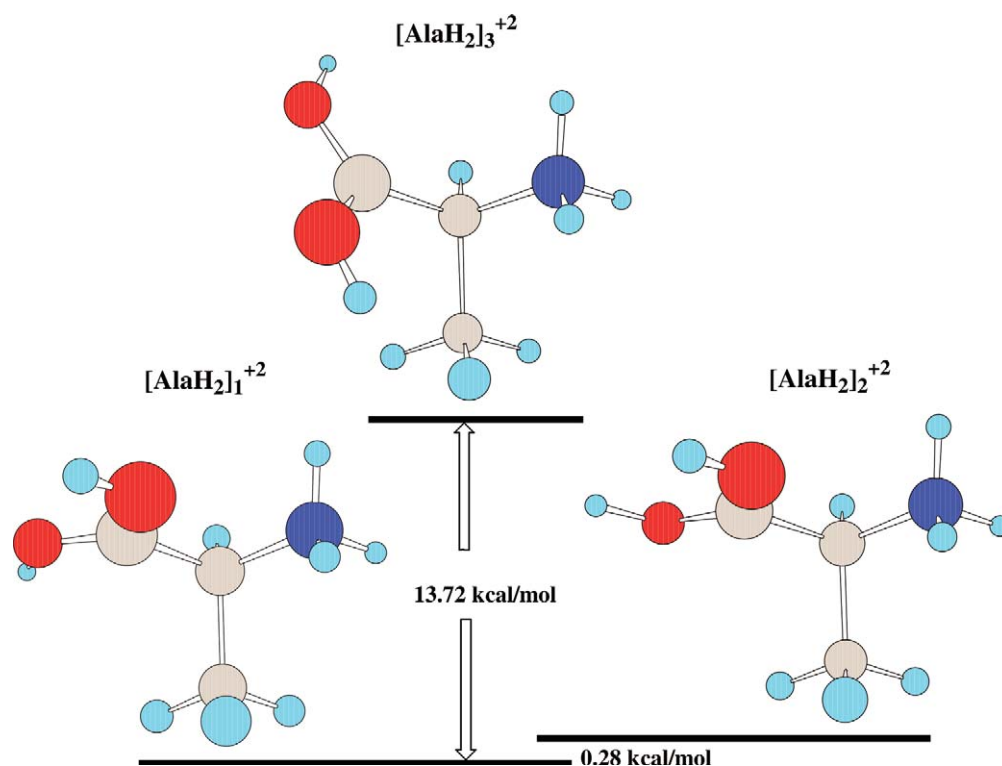


**FIGURE 2.** Two most stable protonated isomers of alanine,  $[\text{AlaH}]_1^+ \leq k \leq 2$ , having the  $\text{NH}_3^+$  group. Note that  $[\text{AlaH}]_2^+ = \mathfrak{P}(\text{Ala-3})$ . Their B3LYP/6-311++G(3df,3pd) ZPE-corrected energy offset comprises of  $7.5 \text{ kcal mol}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

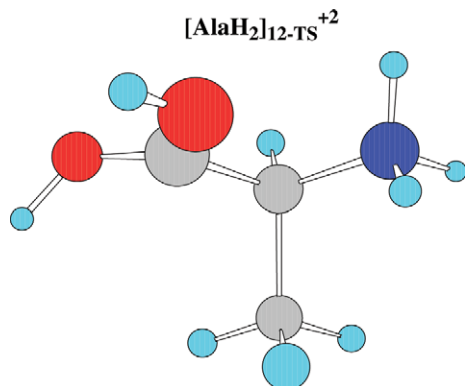
## 5. The Last and Concluding Section

This is the last, except the following two Appendices, but not the least important Section of

this work which addresses few intricate features of protonation. Protonation is one of the most natural and one of the most important processes that occur in the nature and that we observe and measure in terms of the proton affinity. Literally to



**FIGURE 3.** Three stable diprotonated isomers of alanine  $[\text{AlaH}_2]_1^{+2} \leq k \leq 3$ . Their B3LYP/6-311++G(3df,3pd) order of relative stability in the gas phase is given by the ZPE-corrected energy difference  $\Delta E$  (in  $\text{kcal mol}^{-1}$ ) w.r.t. the ground-state isomer  $[\text{AlaH}_2]_1^{+2}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**FIGURE 4.** The transition-state structure which links  $[\text{AlaH}_2]_1^{+2}$  and  $[\text{AlaH}_2]_2^{+2}$  and which is identified at the B3LYP/6-311++G(3df,3pd) computational level. Its transition mode describing the hindered rotation of the distant OH group is characterized by the frequency  $\nu_{\text{tr}} = 730i \text{ cm}^{-1}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

say, protonation is in a sense some “engine” that governs the surrounding molecular world, accomplishing two missions: destruction or creation, which are survived largely due to the repulsive Coulomb potential that is bifunctional as well. The thoughts and propositions which are presented in this work outline our perception of such molecular process that mostly takes place throughout observation and measurement of the key, “macroscopic”-like quantity that determines this process, the proton affinity, leaving beyond the scene myriads of other process which altogether constitute what we mean under the term protonation. Among them are:

- Existence of variety of isomers which order of relative stability can in general be changed under protonation;
- Existence of variety of different protonation sites;
- Protonated activation of a bond and its possible rupture;
- Stability of protonated species;
- Relationship between the bonding manifolds of a parent multielectron system and its protonated form that invalidates the concept of the proton affinity and thus outlines its range.

Closing this Section and hence Part I, we propose the following

**Conjecture:** Protonation of a closed-shell multielectron neutral system lowers its HOMO and LUMO and hence widens the HOMO-LUMO gap.

## Appendix A

### BOUND-STATE PROBLEM FOR ATTRACTIVE INVERSE SQUARE POTENTIAL REVISITED

An attractive inverse square potential  $U_g(r) = -g/r^2$  with  $g > 0$  belongs to the class of singular potentials, and, in particular, regarding the uncertainty principle, to its transition-type subclass [56]. This class continues to deserve the broad attention (see Refs. [56, 57]) that, in particular, focuses on the potential  $U_g(r)$  as the source of big debates in the literature [53, 56, 58–79] arisen around the problem of whether  $U_g$  possesses bound states and whether the well-known von Neumann condition of square integrability [80] (see also [61c]) would be sufficient enough to determine them unambiguously? This Appendix is an attempt to resolve this problem and to discuss its impact on the related issues such as a “falling” of particle of mass  $m$  onto the centre of the inverse cube central force field  $2g/r^3$ , the uncertainty relation, and the virial theorem.

The Schrödinger equation (1) taken in a more explicit form  $H_g \Psi = E[\Psi] \Psi$  with the Hamiltonian  $H_g = T + U_g \equiv -(\hbar^2/2m) \nabla_{\mathbf{r}}^2 + U_g(r)$  reduces to the textbook effective radial equation for  $\psi = r\Psi$ ,

$$\psi_i''(r) + \left(\frac{g_l}{r^2} - \varepsilon_i^2\right)\psi_i(r) = 0, \quad (\text{A1})$$

with the imposed Dirichlet-type boundary condition, where  $g_l = (2mg/\hbar^2) - l(l+1)$  and  $\varepsilon^2 = -2mE/\hbar^2$ . Prime over designates the derivative with respect to  $r$ . Upon substituting  $\psi_i(r) = r^{1/2}\varphi_i(\varepsilon_i r)$  into (A1), the latter is further transformed into the equation for modified Bessel functions,

$$z^2\varphi'' + z\varphi' - (z^2 + v^2)\varphi = 0, \quad (\text{A2})$$

where  $Z = \varepsilon r$  and  $v^2 = (1/4) - g_l = (l+1/2)^2 - (2mg/\hbar^2)$ . The bound-state eigenvalue problem (A1) is valid for positive  $g_l$ . If  $g_l \neq 1/4$ , Eq. (A2) possesses two independent solutions,  $I_v(z)$  and  $I_{-v}(z)$ , ([81], Section 9.6) depending on  $\varepsilon$  throughout the argument. Regarding  $v$ , the admissible  $g_l$  might be divided into the following domains: (Ai)

$g_l < 1/4$ ,  $v$  is positive and less than a half; (Aii)  $g_l = 1/4$  and  $v = 0$ ; and (Aiii)  $g_l > 1/4$ ,  $v$  becomes purely imaginary. In the case (Aii), the unique eigenfunction  $I_0 \varepsilon r$  diverges at infinity and, thus, is not square integrable ([81], Section 9.6 and Eq. (9.6.16)).

Domain (Ai) corresponds to the “weak” attractiveness of the inverse square potential  $U_g(r)$  [56, 58, 62, 63, 65–67, 69–72]. The general solution of Eq. (A2) is sought in the form

$$\varphi(z) = c_+ I_\nu(z) + c_- I_{-\nu}(z). \quad (\text{A3})$$

The familiar behavior of  $I_{\pm\nu}(z)$  at infinity [81] renders that  $\varphi(\infty) = 0$  takes place if  $c_+ = -c_-$ . Thereby  $\varphi(z) = AK_\nu(z)$  where  $A$  is numerical constant and  $K_\nu$  is modified Bessel function. Therefore,

$$\psi(r) = Ar^{1/2} K_\nu(\varepsilon r). \quad (\text{A4})$$

Relying on the known behavior of  $K_\nu(z)$  in the neighborhood of  $z = 0$  ([81], Eq. (9.6.9)) and the fact that  $\nu < 1/2$ , one finds that in the limit of small  $r$ ,  $\psi(r)$  in the form (A4) is given by sum of two solutions,  $\psi(r) \simeq A_1 r^{1/2+\nu} + A_2 r^{1/2-\nu}$ . Both these solutions are square integrable near the origin, and thus, no one should be discarded in favor of another, in contrast to the conclusion in [63c] where the authors misapplied a square integrability at the origin to  $\Psi = \psi/r$  rather than to  $\psi$ .

$\psi(r)$  in (A4) is everywhere square integrable, positive for all  $r \neq 0$  thanks to that  $K_\nu(z)$  has no zeros for real  $\nu$  and  $r$ . This is interpreted as existence of single bound state for “weakly” attractive  $U_g(r)$ . It was therefore thought [58, 65–76] that, first,  $H_g$  loses its self-adjointness on this class of solutions and, second, that the condition of square integrability appears insufficient to resolve the bound-state eigenvalue problem in this case. In the other words, the von Neumann condition mismanages with quantization of energy levels. It was revealed that absence of quantization [56, 57] is linked to the singularity of  $U_g$  at the origin. The final conclusion in the related literature is that the condition of square integrability must be supplied by additional one(s) in order to quantize energy levels.

A “strong” attractiveness of  $U_g(r)$  is realized on the domain (Aiii) of  $g_l$ .  $v$  becomes there imaginary,  $v = ip$ ,  $p$  is real. General solution of Eq. (A1) is searched then in such a form,

$$\psi_m(r) = r^{1/2} [c_{+m} I_{ip}(\varepsilon_m r) + c_{-m} I_{-ip}(\varepsilon_m r)]. \quad (\text{A5})$$

At the origin  $\psi_m$  shows the following behavior,

$$\begin{aligned} \psi_m(r) &\simeq r^{1/2} \left[ \frac{c_{+m} e^{ip \ln \varepsilon_m}}{2^p \Gamma(1+ip)} e^{ip \ln r} + \frac{c_{-m} e^{-ip \ln \varepsilon_m}}{2^{-p} \Gamma(1-ip)} e^{-ip \ln r} \right] \\ &= c_{+m} \left( \frac{r \sinh \pi p}{\pi p} \right)^{1/2} e^{i\psi_m} [\cos \Phi_m \\ &\quad + \rho_m \cos(\chi_m - \Phi_m)] + i [\sin \Phi_m + \rho_m \sin(\chi_m - \Phi_m)] \end{aligned} \quad (\text{A6})$$

where  $\Gamma(1 \pm p) = (\pi p / \sinh \pi p)^{1/2} e^{\pm i\varphi}$ ,  $\delta_m = c_{-m}/c_{+m} = \rho_m e^{i\chi_m}$ , and  $c_{+m} = |c_{+m}| \exp\{i\psi_m\}$ , and where  $\Phi_m = p \ln(\varepsilon_m r/2)$ . Focusing on the current-less condition of  $\psi_m(r)$  at the origin,

$$J_m = [\bar{\psi}_m(r) \psi'_m(r) - \bar{\psi}'_m(r) \psi_m(r)]_{r=0} = 0, \quad (\text{A7})$$

one obtains in straightforward way that

$$J_m = \frac{2i \sin h \pi p}{\pi p} |c_{+m}|^2 (1 - \rho_m^2). \quad (\text{A8})$$

Hence, Eq. (A7) takes place for  $\rho_m = 1$ , or for imaginary  $\delta_m$ . This yields

$$\begin{aligned} \psi_m(r)_{r \sim 0} &\simeq 2c_{+m} e^{i\chi_m/2} \sqrt{\frac{r \sin h \pi p}{\pi p}} \cos[p \ln(\varepsilon_m r/2) \\ &\quad - (\chi_m/2)]. \end{aligned} \quad (\text{A9})$$

Therefore,  $\psi_m(r)$  vanishes at  $r = 0$ , and hence, Eq. (A5) can be rewritten as

$$\psi_m(r) = c_{+m} r^{1/2} [I_{ip}(\varepsilon_m r) + e^{i\chi_m} I_{-ip}(\varepsilon_m r)]. \quad (\text{A10})$$

Let us now turn to deal with asymptotic behavior of  $\psi_m(r)$  at infinity. Equation (A10) demonstrates that at infinity,

$$\begin{aligned} \psi_m(r) &\simeq -\frac{ic_{+m}}{\sqrt{2\pi\varepsilon_m}} \{e^{\varepsilon_m r + i\pi/2} [1 + e^{i\chi_m}] \\ &\quad + e^{-\varepsilon_m r} [e^{ip\pi} + e^{i\chi_m - ip\pi}]\} \\ &= \sqrt{\frac{2}{\pi\varepsilon_m}} c_{+m} \sin(p\pi) e^{-\varepsilon_m r} \end{aligned} \quad (\text{A11})$$

where in the last line  $\chi_m = \pi$ . This value of  $\chi_m$  transforms  $\psi_m(r)$  into the form similar to the case of “weakly” attractive  $U_g(r)$ , viz.,

$$\psi_m(r) = A_m r^{1/2} K_{ip}(\varepsilon_m r) \quad (\text{A12})$$



where  $A_m$  is numerical coefficient. One notes that  $K_\nu(z)$  is real for real positive  $z$  and for purely imaginary  $\nu$ . (A12) then simplifies (A9), viz.

$$\psi_m(r)_{r \sim 0} \simeq 2ic_{+m} \sqrt{\frac{r \sinh \pi p}{\pi p}} \sin \left[ p \ln \left( \frac{\varepsilon_m r}{2} \right) \right]. \quad (\text{A13})$$

Again, as for a “weak” attractiveness, in the neighborhood of the origin,  $\psi_m$  is given by sum of two solutions both of which converge regularly to zero and, thus, both should be treated at equal rights. This contradicts to the statement [63d] made in terms of  $\Psi_m$  whose square integrability at the origin is not so necessary as that of  $\psi_m$ . However, in contrast to the former case with real  $\nu$ , it follows from (A13) that  $\psi_m$  oscillates near the origin. Therefore, the eigenfunction (A12) possesses zeros and takes thus both signs.

We now suggest that for a given value of  $l$ , there exist at least two eigenfunctions, say,  $\psi_m(r)$  and  $\psi_n$ , of Eq. (A1) corresponding to different eigenenergies,  $\varepsilon_m^2$  and  $\varepsilon_n^2$ , respectively. If, by the assumption,  $H_g$  is self-adjoint, these eigenfunctions are mutually orthogonal to each other. In particular, from Eq. (A1) one readily obtains (see [60]) that

$$\int_0^\infty dr \bar{\psi}_n(r) \psi_m(r) = (\varepsilon_m^2 - \varepsilon_n^2)^{-1} [\bar{\psi}_n(r) \psi'_m(r) - \bar{\psi}'_n(r) \psi_m(r)]_0^\infty. \quad (\text{A14})$$

To keep this pair of eigenfunctions being orthogonal requires that

$$\bar{\psi}_n(0) \psi'_m(0) - \bar{\psi}'_n(0) \psi_m(0) = 0. \quad (\text{A15})$$

Let us insert Eq. (A13) into Eq. (A15). The result appears the following,

$$\sin[p \ln(\varepsilon_m/\varepsilon_n)] = 0. \quad (\text{A16})$$

Equation (A16) is, in fact, the quantization of energy for the “strongly” attractive potential  $U_g$ . This quantization is given in terms of the ratio of the adjacent energy eigenvalues. It is equivalent to that

$$E_n = -\beta_p e^{2\pi n/p} \quad (\text{A17})$$

where  $\beta_p$  is any positive constant that leads to an arbitrariness in the overall scale of energy. One concludes that the bound-state energy spectrum

ranges from zero to minus infinity and actually is unbounded below [60]. This implies (see [56, 60, 63d, 65]) that being in the ground state, particle becomes localized in rather small region near the origin, that is, in other words, it “falls” onto the center.

The time-independent Schrödinger equation  $H\Psi = E[\Psi]\Psi$  is deducible from the stationary quantum variational principle to which, in fact, the mentioned von Neumann condition is directly addressed. This principle relied on the Rayleigh-Ritz quotient  $E[\Psi] = \langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$  demands to specify the domain  $D(H)$  of admissible functions  $\Psi \in D(H)$  such that  $E[\Psi]$  is well defined. Instead of  $D(H)$ , one introduces  $\{D\}(H_g)$  of admissible bound-state wave functions  $\psi = r\Psi$ . Speaking generally, this domain  $\{D\}(H_g)$  is fully determined by the following three conditions [80b, 75c]:

- AI.** Square integrability condition:  $\psi \in L^2(0, \infty)$ ;
- AII.** Kinetic energy condition:  $\mathbf{p}\psi \in L^2(0, \infty)$ ,  $\mathbf{p} = -i\hbar\nabla_r$ ;
- AIII.** Potential energy condition:  $U_g\psi \in L^2(0, \infty)$ .

All these conditions were first settled together by J. von Neumann [80b] and it is naturally to suggest that they must bear his name. At this stance, the condition of square integrability, that is precisely the above condition **AI** of square integrability of  $\psi$  on the interval  $[0, \infty)$ , is not sufficient in general to determine a bound spectrum of an arbitrary Hamiltonian and that is why, the answer on the question posed at the beginning is negative indeed. The condition **AII** narrows  $L^2(0, \infty)$  to the Sobolev space  $D(\Delta) = H^{(1)}(0, \infty)$  (see Refs. [80c, 82, 83]) where for any square integrable  $\psi$ ,  $\Delta^{1/2}\psi$  is square integrable as well where  $\Delta$  is the Laplacian operator. It expresses the boundedness of the expectation value of the kinetic energy operator  $T$  [71d, 63c]. The condition **AIII** determines the domain  $D(U_g)$  of the real multiplicative operator  $U_g$  that consists of all such  $\psi$  from  $L^2(0, \infty)$  that  $U_g \psi \in L^2$  [83]. For typical quantum Hamiltonians, the last two conditions always subordinate the condition of square integrability. This can be easily shown by multiplying the corresponding Schrödinger equation  $H\Psi = E[\Psi]\Psi$  by  $\bar{\Psi}$  and integrating further the resultant one.

One easily verifies that for given  $\Psi_k$  either of the type (A4) or (A12),  $\psi_k = r\Psi_k$  obeys the



condition **AI** and not **AII** and **AIII**. In other words,  $\psi_k$  lies in the complement  $H^\perp = L^2(0, \infty) \setminus (H\{1\} \cap D(U_g))$ . Hence, the matrix elements  $\langle \Psi_k | \mathbf{p}^2 \Psi_k \rangle$  and  $\langle \mathbf{p} \Psi_k | \mathbf{p} \Psi_k \rangle$  diverge at the origin. This implies, first, that the kinetic energy operator is not self-adjoint on  $H^\perp$ . Therefore, (A15) that is the key element in the Case analysis [60] is invalid. It is precisely the mutual cancellation of the infinite expectation values of  $T$  and  $U_g$  due to their common divergency at the origin that yields a finite  $\varepsilon_k$  in (A1). It turns out that  $H_g$  is not self-adjoint on  $H^\perp$  and does not represent a physical quantity (see Refs. [80 and 84]). Furthermore, it follows as well that the term  $[\Psi, \Phi]_H = (\hbar^2/2m) \oint_{\partial\mathbb{R}^3} [\bar{\Psi} \nabla_r \Phi - \Phi \nabla_r \bar{\Psi}]$  in the following equation,

$$\langle \Psi | H \Phi \rangle = [\Psi, \Phi]_H + \langle H \Psi | \Phi \rangle, \quad (\text{A18})$$

becomes undefined for all  $\Psi$  of the type (A4) and (A12). For this reason, Eq. (A18) no longer holds on  $H^\perp$  and  $H_g$  is not a symmetric operator there. One thus concludes that there does not exist a self-adjoint extension of  $H_g$  on this domain at all, and moreover,  $H_g$  has no bound states. Domain  $D_g$  should be redefined by imposing some extra condition(s) in order to construct the self-adjoint extension(s) of  $H_g$  there. Because all troubles mentioned above are caused by divergence of the expectation values of  $T$  and  $U_g$  at the origin, a hint to do so is to make an infinite core cut off at any finite distance  $a > 0$  (see Ref. [70], for the alternative approach see Refs. [78, 79, 85]). This leads, first, to that the square integrability is now required in  $L(a, \infty)$  and, second, to that the kinetic and potential energy conditions subordinate that of square integrability. It was shown in [70] that the infinite core cut off at any finite distance does not affect the total infinite number of bound states, rather it shifts the energy levels. Hence, in other words, the tail of  $U_g$  merges an infinite number of bound states whatever is its shape near the origin. It is just the solution of the problem posed by Bohm in his book [75b] (see also Ref. [63e]).

Let us now discuss briefly some issues related to the quantum behavior of particle in the potential  $U_g$ . These are the virial theorem, the Heisenberg uncertainty principle, and a “falling” particle onto the potential center. Their discussions in the literature are based on the tacit assumption of existing of the least bound state. Our case shows the breakdown of this assumption. Therefore, on one hand, the standard derivation of the virial

theorem via scaling of a wave function is not applicable. On the other hand, assuming that the bound state of the type (A4) or (A12) does exist, we have already shown that the expectation value of  $U_g$  in this state is unbounded below. Therefore, the quantum virial theorem no longer holds [86]. Let us go further. As seen from the standard derivation of uncertainties in  $\mathbf{p}$  and  $\mathbf{r}$  (see, e.g., Ref. [63b, 75e, 86]), this procedure is no longer applicable for the potential  $U_g$  for the same reason. Thus, the discussion of their uncertainty correlation in the corresponding literature [56, 63b, 65] is misleading. Moreover, the definition of  $U_g$  as the transition-type operator that was relied on the analysis of the uncertainty [56b] is obviously failed. The same concerns the concept of “falling” of particle onto the centre in the inverse cube central force field  $2g/r^3$  [63b, c].

We therefore conclude that the longstanding problem of sufficiency of the von Neumann condition of square integrability to determine uniquely the bound spectrum of the attractive inverse square potential is resolved. There are, in fact, two original von Neumann conditions [80b] to prescribe  $D(H)$  in  $L^2(\mathbb{R}^3)$  of admissible bound-state wave functions  $\Psi$  of an arbitrary Hamiltonian  $H$ . One is that  $\Psi$  should be square integrable, whereas the second one is that  $\mathbf{p}\Psi$  does, too. For typical quantum Hamiltonians, the second condition always subordinates the former one. This can be shown by multiplying the corresponding Schrödinger equation by  $\bar{\Psi}$  and further integrating. Although, speaking rigorously, one cannot give a priority to the former condition comparing with the second one. In the case of  $H = H_g$ , the condition of  $\mathbf{p}\Psi$  to belong to  $L^2(\mathbb{R}^3)$  so narrows the Hilbert space  $L^2(\mathbb{R}^3)$  to the Sobolev space  $H^{(1)}(\mathbb{R}^3)$  that “washes” out all bound-state eigenfunctions of the Schrödinger equation from  $H^{(1)}(\mathbb{R}^3)$  subject to the Dirichlet-type boundary condition.

## Appendix B

### COMPUTATIONAL METHODOLOGY

All computations of the present work were performed by means of the GAUSSIAN 03 package of quantum chemical programs [87] within the HF, MP2, and the DF B3LYP methods in conjunction with the 311++G(3df,3pd) basis set.

### ACKNOWLEDGMENTS

The author thanks his friends and colleagues for interesting discussions of the concepts of

protonation and the proton affinity. The author thanks Kaline Coutinho for the kind invitation to contribute to the *International Journal of Quantum Chemistry* Festschrift dedicated to 60th birthday of Sylvio Canuto and with the pleasure proposes this work on the concepts of protonation and protonation which are, as well known, tightly linked to the hydrogen bonding theory, one of the main themes of Sylvio Canuto's research for many years. The computational facilities were provided by the CESCA Supercomputing Centre (Barcelona, Spain) with the kind support of Javier Luque and by the GRID Computational Centre (Kiev, Ukraine).

## References

1. Rutherford, E. *Philos Mag* 1911, 21, 669.
2. Hermann, A. *The Genesis of Quantum Theory* (1899–1913); MIT Press: Cambridge, MA; 1971; p 149.
3. (a) Jammer, M. *The Conceptual Development of Quantum Mechanics*; McGraw-Hill: New York, 1966; (b) Heilbron, J. L. *Am J Phys* 1981, 49, 223; (c) Behrens, C. E. *Am J Phys* 1943, 11, 135; (d) American Physical Society. *This Month in Physics History*. May, 1911: Rutherford and the Discovery of the Atomic Nucleus, *APS News*, 2006, p 2; (e) Kalinski, M.; Eberly, J. H.; West, J. A.; Stroud, C. R., Jr. *Phys Rev A* 2003, 67, 032503; (f) Chen, G.; Ding, Z.; Hsu, S.-B.; Kim, M.; Zhou, J. *J Math Phys* 2006, 47, 022107; (g) Ackermann, D.; Simon, H. *Physics* 2009, 2, 101.
4. Bertrand, J. *C R Acad Sci* 1873, 77, 849.
5. Landau, L.; Lifshitz, E. *Classical Mechanics*; Pergamon Press: Oxford, UK, 1976; Section 14.
6. ter Haar, D. *Elements of Hamiltonian Mechanics*; Pergamon Press: Oxford, 1961; Section 1.2.
7. Landau, L. D.; Lifshitz, E. *Quantum Mechanics, Non-Relativistic Theory*; Pergamon: Oxford, 1958; Sections 18, 35.
8. Bohr, N. *Philos Mag* 1913, 26, 857.
9. Kienberger, R.; Goulielmakis, E.; Uiberacker, M.; Baltuska, A.; Yakovlev, V.; Bammer, F.; Scrinzi, A.; Westerwalbesloh, Th.; Kleineberg, U.; Heinzmann, U.; Drescher, M.; Krausz, F. *Nature* 2004, 427, 817.
10. Bubin, S.; Leonarski, F.; Stanke, M.; Adamowicz, L. *J Chem Phys* 130: 124120, 2009.
11. Nelson, J. B.; Tabisz, G. C. *Phys Rev A* 1983, 28, 2157.
12. (a) Erickson, G. W. *J Phys Chem Ref Data* 1977, 6, 831; (b) Strasburger, K. *J Chem Phys* 2009, 131, 134103.
13. A. Einstein. *Ann Phys* (Leipzig) 1905, 17, 549.
14. Kryachko, E. S.; Ludeña, E. V. *Energy Density Functional Theory of Many-Electron Systems*; Kluwer: Dordrecht, 1990.
15. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960.
16. (a) Löwdin, P.-O. In *Molecules in Physics, Chemistry, and Biology*; Maruani, J., Ed.; Kluwer: Dordrecht, 1988; Vol. II, p 3; (b) Löwdin, P.-O. *J Mol Struct (Theochem)* 1991, 230, 13.
17. (a) Woolley, R. G.; Sutcliffe, B. T. In *Fundamental World of Quantum Chemistry. A Tribute to the Memory of Per-Olov Löwdin*; Brändas, E. J., Kryachko, E. S., Eds.; Kluwer: Dordrecht, 2003; Vol. I, p 21; (b) Sutcliffe, B. *Int J Quantum Chem* 2002, 90, 66; (c) Kryachko, E. S. *Int J Quantum Chem* 2008, 108, 1930; (d) Leroy G. *Int J Quantum Chem* 1983, 23, 271, and references therein.
18. Kato, T. *Trans Am Math Soc* 1951, 70, 212.
19. Zhislin, G. M. *Trudy Moskovskogo Matematicheskogo Obschestva* 1960, 9, 81.
20. (a) Uchiyama, J. *Pub Res Inst Math Sci Kyoto A* 1967, 2, 117; (b) Simon, B. *Quantum Mechanics for Hamiltonians Defined as Quadratic Forms*; Princeton University Press: Princeton, 1971; (c) Reed, M.; Simon, B. *Methods of Modern Mathematical Physics, Vol. 4: Analysis of Operators*, 1st ed.; Academic Press: New York, 1978; (d) Thirring, W. A. *Course in Mathematical Physics, Vol. 3, Quantum Mechanics of Atoms and Molecules*; Springer: New York, 1981.
21. Hill, R. N. *J Math Phys* 1977, 18, 2316.
22. (a) Huber, K. P.; Herzberg, G. *Constants of Diatomic Molecules*; van Nostrand-Reinhold: New York, 1979; (b) Cohen, S.; Hiskes, J. R.; Riddell, R. J. *Phys Rev* 1960, 119, 1025; (c) Wind, H. *J Chem Phys* 1965, 42, 2371; (d) Peek, J. M. *J Chem Phys* 1965, 43, 3004; (e) Patel, J. J. *J Chem Phys* 1967, 47, 770; (f) Hu S. X.; Collins L. A.; Schneider, B. I. *Phys Rev A* 2009, 80, 023426.
23. Chandrasekhar, S. *Truth and Beauty*; The University of Chicago Press: Chicago, 1987.
24. Pekeris, C. L. *Phys Rev* 1958, 112, 1649.
25. (a) Kolos, W.; Szalewicz, K.; Monkhorst, H. J. *J Chem Phys* 1986, 84, 3278, and references therein; (b) Richard, J.-M.; Frohlich, J.; Graf, G.-M.; Seifert, M. *Phys Rev Lett* 1993, 71, 1332; (c) Heitler, W.; London, F. *Z Phys* 1927, 44, 455; (d) Kryachko, E. S. *Int J Quantum Chem* 2008, 108, 198.
26. Lieb, E. H. *Bull Am Math Soc* 1990, 22, 1.
27. (a) Dyson, F. J.; Lenard, A. *J Math Phys* 1967, 8, 423; (b) Dyson, F. J.; Lenard, A. *J Math Phys* 1968, 9, 698.
28. Lenard, A. *Lect Notes Phys* 1973, 20, 114.
29. Lieb, E. H.; Thirring, W. In *Studies in Mathematical Physics, Essays in Honor of Valentine Bargmann*; Lieb, E. H.; Simon, B.; Wightman, A., Eds.; Princeton University Press: Princeton, NJ, 1976; p 269.
30. (a) Simenog, I. V. *Teor Mat Fiz* 1974, 20, 235; (b) Armour, E. A. G.; Richard, J.-M.; Varga, K. *Phys Rep* 2005, 413, 1; (c) Ballenegger, V.; Martin, Ph. A. *Physica A* 2002, 306, 59; (d) Rebane T. K. *Phys Atom Nucl* 2009, 72, 55; (e) Simenog, I. V.; Bidasyuk, Yu. M.; Grinyuk, B. E.; Kuzmenko, M. V. *Ukrainian J Phys* 2007, 52, 77; (f) Simenog, I. V.; Bidasyuk, Y. M.; Kuzmenko, M. V.; Khryapa, V. M. *Ukrainian J Phys* 2009, 54, 881, and references therein.
31. Hunziker, W. *Helv Phys Acta* 1966, 39, 451.
32. van Winter, C. *Mat-Fys Skr Danske Vid Selsk* 1964, 2, 1.
33. Jorgens, K.; Weidmann, J. *Spectral Properties of Hamiltonian Operators*; Springer: Berlin, 1973.
34. Solovej, J. P. *Commun Math Phys* 1990, 130, 185.
35. Lieb, E. H.; Thirring, W. E. *Phys Rev A* 1986, 34, 40.
36. Barbaroux, J.-M.; Chen, T.; Vugalter, S. *Ann Henri Poincaré* 2003, 4, 1101.
37. Lewin, M. *Ann Henri Poincaré* 2004, 5, 477.

38. Lewin, M. *Arch Rat Mech Anal* 2004, 171, 83.
39. Stowasser, R.; Hoffmann, R. *J Am Chem Soc* 1999, 121, 3414.
40. Eyring, H.; Polanyi, M. *Z Phys Chem B* 1935, 12, 4.
41. Sax, A. F., Ed. *Potential Energy Surfaces, Lecture Notes in Chemistry*; Springer: Berlin, 1999; Vol. 71.
42. (a) Suenram, R. D.; Lovas, F. J. *J. Am Chem Soc* 1980, 102, 7180; (b) Filsinger, F.; Erlekam, U.; von Helden, G.; Küpper, J.; Meijer, G. *Phys Rev Lett* 2008, 100, 133003; (c) Killblane, C.; Gao, Y.; Shao, N.; Zeng, X. C. *J Phys Chem A* 2009, 113, 8839, and references therein; (d) Gruene, P.; Rayner, D. M.; Redlich, B.; van der Meer, A. F. G.; Lyon, J. T.; Meijer, G.; Fielicke, A. *Science* 2008, 321, 674; (e) Xing, X.; Yoon, B.; Landman, U.; Parks, J. H. *Phys Rev B* 2006, 74, 165423; (f) Huang, W.; Bulusu, S.; Pal, R.; Zeng, X. C.; Wang, L.-S. *ACS Nano* 2009, 3, 1225.
43. (a) Tomioka, H.; Iwamoto E.; Itakura H.; Hirai K. *Nature* 2001, 412, 626; (b) Roth, H. D. *Nature* 2001, 412, 598.
44. IUPAC. *Compendium of Chemical Terminology*, 2nd ed. (The "Gold Book." Compiled by McNaught, A. D.; Wilkinson, A.), Blackwell Scientific Publications: Oxford, 1997.
45. (a) McCullough, E. A., Jr. *J Chem Phys* 1975, 62, 3991; (b) Heinemann, D.; Fricke, B.; Kolb, D. *Phys Rev A* 1988, 38, 4994.
46. (a) McWeeny, R.; Sutcliffe, B. T. *Methods of Molecular Quantum Mechanics*; Academic Press: London, 1969; (b) Paldus, J. In *Theory and Applications of Computational Chemistry: The First Forty Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, 2005; Chapter 7, p 115, and references therein.
47. (a) Lieb, E. H.; Simon, B. *Commun Math Phys* 1977, 53, 185; (b) Lieb, E. H.; Simon, B. *J Chem Phys* 1974, 61, 735.
48. Lions, P.-L. *Commun Math Phys* 1987, 109, 33.
49. Le Bris, C.; Lions, P.-L. *Bull Am Math Soc* 1990, 42, 1.
50. (a) Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 2ff; (b) Dixon D. A.; Lias S. G. In *Molecular Structure and Energetics*; Liebman, J. F.; Greenberg A, Eds.; VCH: Deerfield Beach, FL, 1987; Vol 2, p 269; (c) Hunter, E. P. L.; Lias, S. G. *J Phys Chem Ref Data* 1998, 27, 413; (d) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J Phys Chem Ref Data* 1988, 14(Suppl 1), 1; (e) Meot-Ner (Mautner), M.; Sieck, L. W. *J Am Chem Soc* 1991, 113, 4448; (f) Smith, B. J.; Radom, L. *J Am Chem Soc* 1993, 115, 4885; (g) Szulejko, J. E.; MacMahon, T. B. *J Am Chem Soc* 1993, 115, 7839; (h) Meot-Ner (Mautner), M. *Int J Mass Spectrom* 2003, 227, 525; (i) Deakyne, C. A. *Int J Mass Spectrom* 2003, 227, 601; (j) Vianello, R.; Maksic, Z. B. *J Phys Chem A* 2007, 111, 11718; (k) Kryachko, E. S. *Int J Quantum Chem* 2010, 110, 104 for a current work, and references therein; (l) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J Phys Chem Ref Data* 1984, 13 695.
51. (a) Nold, M. J.; Wesdemiotis, C.; Yalcin, T.; Harrison, A. G. *Int J Mass Spectrom Ion Processes* 1997, 164, 137; (b) Nold, M. J.; Cerda, B. A.; Wesdemiotis, C. *J Am Soc Mass Spectrom* 1999, 10, 1; (c) Aribi, H. E.; Rodriguez, C. F.; Almeida, D. R. P.; Ling, Y.; Mak, W. W.-N.; Hopkinson, A. C.; Siu, R. W. M. *J Am Chem Soc* 2003, 125, 9229; (d) Topol I. A.; Burt S. L.; Toscano M.; Russo N. *J Mol Struct (Theochem)* 1998, 430, 41; (e) Topol I. A.; Burt S. K.; Russo N.; Toscano, M. *J Am Soc Mass Spectrom* 1999, 10, 318.
52. (a) Selvarengan, P.; Kolandaivel, P. *J Mol Struct (Theochem)* 2004, 671, 77; (b) Marino, T.; Russo, N.; Toscano, M. *Inorg Chem* 2001, 40, 6439; (c) Stepanian, S. G.; Reva, I. D.; Radchenko, E. D.; Adamowicz, L. *J Phys Chem A* 1998, 102, 4623.
53. (a) Englefield, M. J. *Proc Phys Soc London* 1964, 83, 519; (b) Vogt, E.; Wannier, G. H. *Phys Rev* 1954, 95, 1190.
54. Morales, G. M.; Jiang, P.; Yuan, S.; Lee, Y.; Sanchez, A.; You, W.; Yu, L. *J Am Chem Soc* 2005, 127, 10456.
55. Moylan, C. R.; Brauman, J. I. *Ann Rev Phys Chem* 1983, 34, 187, and references therein.
56. (a) Frank, W. M.; Land, D. J.; Spector, R. M. *Rev Mod Phys* 1971, 43, 36; (b) p 40 excluding p 39; (c) p 42.
57. (a) Courant, R.; Hilbert, D. *Methods of Theoretical Physics*; Wiley-Interscience: New York, 1953; Vol. I, p 446; (b) Simon, B. *Helv Phys Acta* 1970, 43, 607; (c) Reed, M.; Simon, B. *Methods of Mathematical Physics. Vol. IV: Analysis of Operators*; Academic: New York, 1978; (d) Spector, R. M. *J Math Phys* 1967, 8, 2357.
58. Shortley, G. H. *Phys Rev* 1931, 38, 120.
59. Mott, N. F.; Massey, H. S. *Theory of Atomic Collisions*; Clarendon: Oxford, 1949; p 40.
60. (a) Morse, P. M.; Feshbach, H. *Methods of Theoretical Physics*; McGraw-Hill: New York, 1953; (b) p 1665; (c) p 1114; (d) p 199; (e) p 1666.
61. Kemble, E. C. *The Fundamental Principles of Quantum Mechanics*; McGraw-Hill: New York, 1937; Section 17, p 198.
62. Landau, L. D.; Lifshitz, E. *Quantum Mechanics, Non-Relativistic Theory*; Pergamon: Oxford, 1958; Sections 18, 35, p 117.
63. (a) Morse, P. M.; Feshbach, H. *Methods of Theoretical Physics*; McGraw-Hill: New York, 1953; (b) p 1665; (c) p 199; (d) p 1114, 1666.
64. Scarf, F. L. *Phys Rev* 1958, 109, 2170.
65. Guggenheim, E. A. *Proc Phys Soc London* 1966, 89, 491.
66. Tietz, T. *Nuovo Cim* 1959, 11, 126.
67. Nicholson, A. F. *Aust J Phys* 1962, 15, 174.
68. (a) Spector, R. M. *J Math Phys* 1964, 5, 1185; (b) Nelson, E. *J Math Phys* 1964, 5, 332; (c) Hunziker, W. In *Quantum Theory and Statistical Mechanics. Lectures in Theoretical Physics*; Barut, A. O.; Brittin, W. E.; Gordon and Breach: New York, 1968; Vol. X-A, p 4.
69. Perelomov, A. M.; Popov, V. S. *Teor Mat Fiz* 1970, 4, 48.
70. Ferreira, E.; Sesma, J.; Torres, P. L. *Prog Theory Phys* 1970, 43, 1.
71. Meetz, K. *Nuovo Cim* 1964, 34, 690.
72. Behncke, H. *Nuovo Cim* 1968, 55A, 780.
73. Baz', A. I.; Zel'dovich, Ya. B.; Perelomov, A. M. *Scattering, Reactions and Decays in Non-Relativistic Quantum Mechanics*; Israel Program for Scientific Translation: Jerusalem, 1969.
74. Gupta, K. S.; Rajeev, S. G. *Phys Rev D* 1993, 48, 5940.
75. Bohm, D. *Quantum Theory*; Prentice-Hall: New York, 1951; Section 9.5, p 341; p 178, 186.
76. Park, D. *Introduction to The Quantum Theory*; McGraw-Hill: New York, 1964; p 186ff (Problem 7.27).

77. (a) Gangopadhyaya, A.; Panigrahi, P. K.; Sukhatmel, U. P. *J Phys A: Math Gen* 1994, 27, 4295; (b) Williams, B. W.; Rutherford, J. L.; Lévai, G. *Phys Lett A* 1995, 199, 1.
78. (a) Giri, P. R. *Phys Rev A* 2007, 76, 012114; (b) Gong, J.; Ma, A.; Rice, S. A. *Phys Rev A* 2005, 72, 063410; (c) Hammer, H.-W.; Swingle, B. G. *Ann Phys* 2006, 321, 306.
79. (a) Camblong, H. E.; Epele, L. N.; Fanchiotti, H.; Canal, C. A. G. *Phys Rev Lett* 2001, 87, 220402; (b) Essin, A. M.; Griffiths, D. J. *Am J Phys* 2006, 74, 109; (c) Alhaidari, A. D.; Bahlouli, H. *Phys Rev Lett* 100: 110401, 2008.
80. Neumann, J. V. *Mathematical Foundations of Quantum Mechanics*; Princeton University: Princeton, 1955; p 93, Chapter II, Sections 5–8, (Footnotes 58 and 105).
81. Abramowitz, M.; Stegun, I. A. *Handbook of Mathematical Functions*; Dover: New York, 1972.
82. Neumann, J. V. *Z Math* 1926, 161, 208.
83. Kato, T. *Trans Am Math Soc* 1951, 70, 195; Sections 1, 2, and 5 (last paragraph on p 207).
84. (a) Stone, M. H. *Linear Transformations in Hilbert Space*; American Mathematical Society.: Providence, 1932; Vol. XV; (b) Dunford, N.; Schwartz, J. T. *Linear Operators*; Wiley: New York, 1963; Part II.
85. van Haeringen, H. *J Math Phys* 1978, 19, 2171.
86. Schiff, L. I. *Quantum Mechanics*; McGraw-Hill: New York, 1955.
87. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision C. 02; Gaussian, Inc.: Wallington, CT, 2004.