

Many-electron atoms in the limit of large dimensionality.

Contents

I. Introduction	2
II. S-state of an arbitrary system of several particles bound by Coulomb forces	2
III. Removal of first-order derivatives	5
IV. Large-D limit	8
V. Possible issues for N-electron atoms	9
VI. One-electron atoms	10
VII. Two-electron atoms	11
A. Derivation of large- D limit for two-electron atoms (This section is not necessary because in other section derivations are done in a general case of N electrons)	12
VIII. General case of N-electron atom	14
A. Classical limit for N -electron atom	16
B. Multiple scaling for N -electron atom	19
IX. Possible generalizations of Loeser's model	21
A. Volume of a simplex and its derivatives	25
B. Geometrical properties of a regular simplex	31
References	33

I. INTRODUCTION

First, we consider the large- D limit for S-state of an arbitrary system of several particles bound by Coulomb forces. Then, we consider a particular case of such system which is an atom with infinitely heavy nucleus. We analyze the case of two electrons and determine oscillator quantum numbers both for singlet and triplet states. Then, we discuss generalizations for many-electron atoms. Finally, we consider Bohr-inspired generalization of the Loeser's model.

II. S-STATE OF AN ARBITRARY SYSTEM OF SEVERAL PARTICLES BOUND BY COULOMB FORCES

Although the D -dimensional generalization of Schrödinger equation for a two-body systems like a hydrogen atom or three-body systems like a helium atom or a positive hydrogen ion was comprehensively studied in literature (see for example [11], we found only a few articles dealing with a more general case of several particles [1, 2, 5, 6, 10, 12]. Derivations are straightforward, but lengthy. It is probably the reason that details of derivations were missing in the earlier paper [10]. Here, we express D -dimensional Laplacian in “internal coordinates”. Our derivations basically repeats those of the of the paper [12], see their formulas (6) - (9).

We consider a system of $N + 1$ particles with masses m_α located at points \mathbf{r}_α , where $\alpha = 0, 1, 2, \dots, N$, and $\mathbf{r}_\alpha = (r_\alpha^{(1)}, r_\alpha^{(2)}, \dots, r_\alpha^{(D)})$ is a vector in D -dimensional space. Then, D -dimensional generalization of Schrödinger

equation reads

$$\left(\sum_{\alpha} \frac{\mathbf{p}_{\alpha}^2}{2m_{\alpha}} + \sum_{\substack{\alpha, \beta \\ \alpha < \beta}} \frac{\lambda_{\alpha\beta}}{r_{\alpha\beta}} - E \right) \Psi(\mathbf{r}_0, \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = 0, \quad (1)$$

where $\mathbf{p}_{\alpha} = \frac{\hbar}{i} \left(\frac{\partial}{\partial r_{\alpha}^{(1)}}, \frac{\partial}{\partial r_{\alpha}^{(2)}}, \dots, \frac{\partial}{\partial r_{\alpha}^{(D)}} \right)$ is D -dimensional momentum, $r_{\alpha\beta} = |\mathbf{r}_{\alpha} - \mathbf{r}_{\beta}|$ are distances between particles, and $\lambda_{\alpha\beta}$ are Coulomb force constants.

We restrict ourself to S-states. In S-state, the wavefunction depends only on $N(N+1)/2$ ‘‘internal’’ coordinates that are invariant under rotation of the coordinate system. Here, we use as ‘‘internal’’ coordinates the inter-particle distances,

$$\Psi(\mathbf{r}_0, \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = \psi(r_{01}, r_{02}, \dots, r_{0N}, r_{12}, r_{13}, \dots, r_{1N}, \dots, r_{N-1,N}) \quad (2)$$

In the available literature [1, 2, 5, 6, 10, 12], the authors used a less symmetric choice of ‘‘internal’’ coordinates, namely N distances $r_{0\alpha}$ with $\alpha = 1, 2, \dots, N$ and $N(N-1)/2$ cosines of angles $\gamma_{\alpha\beta} = \frac{r_{0\alpha}^2 + r_{0\beta}^2 - r_{\alpha\beta}^2}{2r_{0\alpha}r_{0\beta}}$ with $\alpha, \beta = 1, 2, \dots, N$. It was motivated by the fact that in physical problems like N -electron atoms one of the particles with large mass (e.g. atomic nucleus) plays a special role. To our opinion, a symmetrical choice of ‘‘internal’’ coordinates, i.e. the choice of entire set of distances instead of a subset of $N(N-1)/2$ distances plus N angles leads to a more compact and simple formulas. Compare, for example, our expression for the Laplacian, equation (9), with the analogous formula (9) from the paper [12].

Calculating first derivatives, we obtain

$$\frac{\partial \psi}{\partial r_{\alpha}^{(i)}} = \sum_{\substack{\beta \\ \beta \neq \alpha}} \frac{\partial r_{\alpha\beta}}{\partial r_{\alpha}^{(i)}} \frac{\partial \psi}{\partial r_{\alpha\beta}} = \sum_{\substack{\beta \\ \beta \neq \alpha}} \frac{r_{\alpha\beta}^{(i)}}{r_{\alpha\beta}} \frac{\partial \psi}{\partial r_{\alpha\beta}}, \quad (3)$$

where $r_{\alpha\beta}^{(i)} = r_{\alpha}^{(i)} - r_{\beta}^{(i)}$. Calculating second derivatives, we obtain

$$\frac{\partial^2 \psi}{\partial r_{\alpha}^{(i)2}} = \sum_{\substack{\beta \\ \beta \neq \alpha}} \frac{1}{r_{\alpha\beta}} \frac{\partial \psi}{\partial r_{\alpha\beta}} + \sum_{\substack{\beta \\ \beta \neq \alpha}} r_{\alpha\beta}^{(i)} \frac{\partial}{\partial r_{\alpha}^{(i)}} \left(\frac{1}{\partial r_{\alpha\beta}} \frac{\partial \psi}{\partial r_{\alpha\beta}} \right). \quad (4)$$

Using equation (3), we could rewrite the second term in equation (4) as

$$\begin{aligned} \sum_{\substack{\beta, \gamma \\ \beta \neq \alpha, \gamma \neq \alpha}} r_{\alpha\beta}^{(i)} r_{\alpha\gamma}^{(i)} \frac{1}{r_{\alpha\gamma}} \frac{\partial}{\partial r_{\alpha\gamma}} \left(\frac{1}{r_{\alpha\beta}} \frac{\partial \psi}{\partial r_{\alpha\beta}} \right) = \\ \sum_{\substack{\beta \\ \beta \neq \alpha}} r_{\alpha\beta}^{(i)} r_{\alpha\beta}^{(i)} \frac{1}{r_{\alpha\beta}} \left(-\frac{1}{r_{\alpha\beta}^2} \right) \frac{\partial \psi}{\partial r_{\alpha\beta}} + \sum_{\substack{\beta, \gamma \\ \beta \neq \alpha, \gamma \neq \alpha}} r_{\alpha\beta}^{(i)} r_{\alpha\gamma}^{(i)} \frac{1}{r_{\alpha\gamma}} \frac{1}{r_{\alpha\beta}} \frac{\partial^2 \psi}{\partial r_{\alpha\gamma} \partial r_{\alpha\beta}}. \end{aligned} \quad (5)$$

Since

$$\mathbf{r}_{\beta\gamma}^2 = (\mathbf{r}_{\alpha\beta} - \mathbf{r}_{\alpha\gamma})^2 = \mathbf{r}_{\alpha\beta}^2 + \mathbf{r}_{\alpha\gamma}^2 - 2(\mathbf{r}_{\alpha\beta}, \mathbf{r}_{\alpha\gamma}), \quad (6)$$

we could express

$$\sum_{i=1}^D r_{\alpha\beta}^{(i)} r_{\alpha\gamma}^{(i)} = (\mathbf{r}_{\alpha\beta}, \mathbf{r}_{\alpha\gamma}) = \frac{1}{2} (\mathbf{r}_{\alpha\beta}^2 + \mathbf{r}_{\alpha\gamma}^2 - \mathbf{r}_{\beta\gamma}^2). \quad (7)$$

Using equation (7) and taking into account equations (4) and (5), we could calculate

$$\begin{aligned} \nabla_{\alpha}^2 \psi = \sum_{i=1}^D \frac{\partial^2 \psi}{\partial r_{\alpha}^{(i)2}} = \sum_{\substack{\beta \\ \beta \neq \alpha}} \frac{D}{r_{\alpha\beta}} \frac{\partial \psi}{\partial r_{\alpha\beta}} - \\ \sum_{\substack{\beta \\ \beta \neq \alpha}} \frac{1}{r_{\alpha\beta}} \frac{\partial \psi}{\partial r_{\alpha\beta}} + \sum_{\substack{\beta, \gamma \\ \beta \neq \alpha, \gamma \neq \alpha}} \frac{r_{\alpha\beta}^2 + r_{\alpha\gamma}^2 - r_{\beta\gamma}^2}{2r_{\alpha\beta} r_{\alpha\gamma}} \frac{\partial^2 \psi}{\partial r_{\alpha\beta} \partial r_{\alpha\gamma}}. \end{aligned} \quad (8)$$

The first term in r.h.s. of equation (8) comes from the first term in equation (4), the second and the third terms come from two terms in equation (5).

We rewrite equation (8) in a more compact form

$$\nabla_{\alpha}^2 \psi = (D-1) \sum_{\substack{\beta \\ \beta \neq \alpha}} \frac{1}{r_{\alpha\beta}} \frac{\partial \psi}{\partial r_{\alpha\beta}} + \sum_{\substack{\beta, \gamma \\ \beta \neq \alpha, \gamma \neq \alpha}} C_{\beta\gamma}^{(\alpha)} \frac{\partial^2 \psi}{\partial r_{\alpha\beta} \partial r_{\alpha\gamma}}, \quad (9)$$

where

$$C_{\beta\gamma}^{(\alpha)} = \frac{r_{\alpha\beta}^2 + r_{\alpha\gamma}^2 - r_{\beta\gamma}^2}{2r_{\alpha\beta}r_{\alpha\gamma}}, \quad (10)$$

which is incidentally an expression for a cosine of the angle between vectors $\mathbf{r}_\alpha - \mathbf{r}_\gamma$ and $\mathbf{r}_\beta - \mathbf{r}_\gamma$.

III. REMOVAL OF FIRST-ORDER DERIVATIVES

This step is in the core of large- D approach, because in the large- D limit it allows to replace the kinetic energy by a centrifugal potential and to determine the energy simply as a minimum of some coordinate function which is the sum of a physical potential and the centrifugal term. It is interesting (this fact remains unnoticed in literature), that the $D \rightarrow \infty$ limit could be determined even without removal of first-order derivatives. Without giving further details, we just mention here that the method reduces to minimization of the Hamiltonian function in respect to both coordinates and momenta variables. In principle, the minimization could be done first over the momenta, and then over the coordinates. Then, minimization over the momenta will lead to a system of linear equations which are essentially equivalent to the equations that appear during the removal of first-order derivatives.

The idea of removing first-order derivatives is to rewrite the Laplacian operator for the modified function which is the initial wave function ψ multiplied by some function of coordinates f ,

$$P(\{r_{\alpha\beta}\}) = f(\{r_{\alpha\beta}\})\psi(\{r_{\alpha\beta}\}). \quad (11)$$

It is known that for two or three particles, the function f could be chosen as some power of the volume of the simplex formed by particles. We shall

prove here, that a similar choice of f , $f = V^\rho$, where V is the volume of N -dimensional simplex formed by $N + 1$ particles, is sufficient for eliminating first-order derivatives.

Let us firstly consider the case of $\alpha = 0$ and rewrite the α -th component of the Laplacian given by equation (9) as

$$\nabla_0^2 \psi = (D - 1) \sum_{\alpha=1}^N \frac{1}{r_\alpha} \frac{\partial \psi}{\partial r_\alpha} + \sum_{\alpha, \beta=1}^N \frac{Q_{\alpha\beta}}{r_\alpha r_\beta} \frac{\partial^2 \psi}{\partial r_\alpha \partial r_\beta}, \quad (12)$$

where we used the same notations $r_\alpha \equiv r_{0\alpha}$ and $Q_{\alpha\beta} = \frac{1}{2} (r_\alpha^2 + r_\beta^2 - r_{\alpha\beta}^2)$ as in Appendix A.

After substitution of $\psi = V^{-\rho} P$ into equation (12), we obtain

$$\begin{aligned} \nabla_0^2 \psi &= (D - 1) \sum_{\alpha} \frac{1}{r_\alpha} \left(V^{-\rho} \frac{\partial P}{\partial r_\alpha} - \rho V^{-\rho-1} \frac{\partial V}{\partial r_\alpha} P \right) \\ &+ \sum_{\alpha, \beta} \frac{Q_{\alpha\beta}}{r_\alpha r_\beta} \left[V^{-\rho} \frac{\partial^2 P}{\partial r_\alpha \partial r_\beta} - \rho V^{-\rho-1} \left(\frac{\partial V}{\partial r_\alpha} \frac{\partial P}{\partial r_\beta} + \frac{\partial P}{\partial r_\alpha} \frac{\partial V}{\partial r_\beta} \right) \right. \\ &\left. + \rho(\rho + 1) V^{-\rho-2} \frac{\partial V}{\partial r_\alpha} \frac{\partial V}{\partial r_\beta} P - \rho V^{-\rho-1} \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta} P \right]. \end{aligned} \quad (13)$$

By equating the coefficient in front of the derivative $\partial P / \partial r_\alpha$ in equation (13) to zero, we obtain

$$\frac{D - 1}{r_\alpha} V^{-\rho} - 2\rho \frac{V^{-\rho-1}}{r_\alpha} \sum_{\beta} \frac{Q_{\alpha\beta}}{r_\beta} \frac{\partial V}{\partial r_\beta} = 0, \quad (14)$$

or, after multiplying equation (14) by $r_\alpha V^{\rho+1}$, in equivalent form

$$(D - 1)V - 2\rho \sum_{\beta} \frac{Q_{\alpha\beta}}{r_\beta} \frac{\partial V}{\partial r_\beta} = 0. \quad (15)$$

Comparing equation (15) with equation (A9) in Appendix A, we could see that equation (15) is satisfied if we set

$$\rho = \frac{D - 1}{2}. \quad (16)$$

After substituting equation (16) into equation (13) linear derivatives disappear, and we obtain

$$\nabla_0^2 \psi = V^{-\frac{D-1}{2}} \left(\sum_{\alpha, \beta} \frac{Q_{\alpha\beta}}{r_\alpha r_\beta} \frac{\partial^2 P}{\partial r_\alpha \partial r_\beta} + v_c^{(0)} P \right), \quad (17)$$

where the component of ‘‘centrifugal potential’’ $v_c^{(0)}$ is given by

$$v_c^{(0)} = -\frac{(D-1)^2}{2V} \sum_{\alpha} \frac{1}{r_\alpha} \frac{\partial V}{\partial r_\alpha} + \frac{D^2-1}{4V^2} \sum_{\alpha, \beta} \frac{Q_{\alpha\beta}}{r_\alpha r_\beta} \frac{\partial V}{\partial r_\alpha} \frac{\partial V}{\partial r_\beta} - \frac{D-1}{2V} \sum_{\alpha, \beta=1}^N \frac{Q_{\alpha\beta}}{r_\alpha r_\beta} \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta}. \quad (18)$$

Using equations (A9) and (A23) from Appendix A, we could perform summation over β in second term and over α, β in third term in equation (18) and obtain

$$\begin{aligned} v_c^{(0)} &= -\frac{(D-1)^2}{2V} \sum_{\alpha} \frac{1}{r_\alpha} \frac{\partial V}{\partial r_\alpha} + \frac{D^2-1}{4V} \sum_{\alpha} \frac{1}{r_\alpha} \frac{\partial V}{\partial r_\alpha} - \frac{D-1}{2} (1-N) \frac{1}{h_0^2} \\ &= -\frac{(D-1)(D-2N-1)}{4V} \sum_{\alpha} \frac{1}{r_\alpha} \frac{\partial V}{\partial r_\alpha}. \end{aligned} \quad (19)$$

Finally, using equation (A15) from Appendix A we obtain

$$v_c^{(0)} = -\frac{(D-1)(D-2N-1)}{4h_0^2}. \quad (20)$$

Since we could always change enumeration of particles so that γ -th particle would become 0-th one, a generalization of equation (17) which is obtained by replacing $0 \rightarrow \gamma$ is valid too,

$$\nabla_\gamma^2 \psi = V^{-\frac{D-1}{2}} \left(\sum_{\alpha, \beta \neq \gamma} C_{\alpha\beta}^{(\gamma)} \frac{\partial^2 P}{\partial r_{\alpha\gamma} \partial r_{\beta\gamma}} - \frac{(D-1)(D-2N-1)}{4h_\gamma^2} P \right), \quad (21)$$

where we used a notation for matrix coefficients $C_{\alpha\beta}^{(\gamma)}$ given by equation (10).

Finally, using equation (8), the kinetic energy multiplied by $V^{\frac{D-1}{2}}$ is expressed as

$$\begin{aligned} T'P \equiv V^{\frac{D-1}{2}}T\psi &= -\frac{\hbar^2}{2}V^{\frac{D-1}{2}}\sum_{\alpha}\frac{\nabla_{\alpha}^2\psi}{m_{\alpha}} \\ &= -\frac{\hbar^2}{2}\sum_{\gamma}\frac{1}{m_{\gamma}}\sum_{\alpha,\beta\neq\gamma}C_{\alpha\beta}^{(\gamma)}\frac{\partial^2P}{\partial r_{\alpha\gamma}\partial r_{\beta\gamma}}+V_cP, \end{aligned} \quad (22)$$

where

$$V_c = \frac{\hbar^2}{8}(D-1)(D-2N-1)\sum_{\gamma}\frac{1}{m_{\gamma}h_{\gamma}^2}. \quad (23)$$

The same formula (without giving details of derivations) was obtained in [4], see their equation (2.36).

IV. LARGE- D LIMIT

It is possible to prove that $E \sim D^{-2}(E_0 + E_1/D + O(1/D^2))$, where coefficients E_0 and E_1 are determined as follows. First, we define an “effective potential” as

$$U = V + \lim_{D \rightarrow \infty} (D^{-2}V_c) = V + U_c, \quad (24)$$

where

$$U_c = \frac{1}{8}\sum_{\gamma}\frac{1}{m_{\gamma}h_{\gamma}^2}. \quad (25)$$

Henceforward, we use units where $\hbar = 1$. Then, zero-order coefficient is determined as

$$E_0 = \min_{\{r_{\alpha\beta}\}} U(\{r_{\alpha\beta}\}). \quad (26)$$

The first-order correction is expressed as

$$E_1 = U_1 + \sum_{i=1}^{N(N+1)/2} \left(\nu_i + \frac{1}{2} \right) \omega_i, \quad (27)$$

where $\{\nu_i\}$ are nonnegative integer numbers that have meaning of oscillator quantum numbers (zeros for the ground state), and $\{\omega_i\}$ are frequencies. The frequencies are determined by a more complicated way [12] by simultaneous diagonalization of two matrixes which elements are coefficients of quadratic forms of second derivatives and second-order Maclaurin expansion of the potential U around its minimum. An additional term U_1 is the first coefficient of $1/D$ -expansion of the quantity D^2V_c . It is taken at the same arguments for which U attains the minimum.

V. POSSIBLE ISSUES FOR N -ELECTRON ATOMS

Henceforward, we shall consider a particular case of Coulomb-force systems with $m_0 = \infty$, $m_\alpha = 1$, $\lambda_{0\alpha} = -1$, $\lambda_{\alpha\beta} = \lambda$, where $\alpha, \beta = 1, 2, \dots, N$. This case corresponds to a neutral atom ($\lambda = 1/N$) or to an ion ($\lambda = 1/Z$, $Z \neq N$) in re-scaled units where nuclear charge is one. We shall use notations $r_{0\alpha} \equiv r_\alpha$, $\pi_{0\alpha} \equiv \pi_\alpha$.

A physical problem could be generalized to an arbitrary dimensionality D in many ways. In order to gain useful information from this generalization, we demand that the particular case of $D = 3$ is equivalent to the physical problem. For many-electron atoms, we consider D -dimensional generalization in the most natural way, by allowing the radius-vectors of electrons to be D -dimensional. It should be noted that in this case the requirement of equivalency of $D = 3$ to the physical problem is not always satisfied. Consider, for example, an atom with 100 electrons. The Schrödinger equation has in this case 300 variables, and some of them, like 3 center of mass coordinates, could be eliminated. In contrast, the D -dimensional generalization, in which

Laplacians are replaced by differential operators given by equation (9), has $100 \times 101/2 = 5050$ independent variables which are inter-particle distances. For sufficiently low dimensionality, inter-particle distances are no longer independent. For example, for two electrons in one dimension, we have always either $r_1 \pm r_{12} = r_2$ or $r_1 + r_2 = r_{12}$. For 100 electrons, it occurs at $D = 3$, so using the equation which is valid for large D is not correct. For the first three atoms, H, He, and Li, the inter-particle distances are mutually independent in three dimensions, and the D -dimensional generalization gives physical result at $D = 3$. For all heavier atoms, the large- D method could be considered just as a “model” to the physical case of $D = 3$.

It should be noted that there exist several issues that obscure the large- D limit for many-electron atoms. For some atoms like boron, the angular momentum is not zero, and the above derivations for S-states are not rigorously applicable. For atoms with $Z > 12$, the global minimum of the effective potential becomes strongly asymmetric. It was disregarded in [10] in favor of a totally symmetric local minimum. Atoms with $n = 3$ -shell electrons, for example Mg, change their ground-state configurations from $1s^2 1p^6 3s^2$ for $D = 3$ to a more compact configuration $1s^2 1p^8$ for $D \geq 4$, which is disregarded here too [10].

VI. ONE-ELECTRON ATOMS

For $N = 1$, there is only one internal coordinate $r_1 \dots$
 $\dots 1/D$ -expansion could be derived in closed form \dots

VII. TWO-ELECTRON ATOMS

For $N = 2$, the Schrödinger equation has 3 independent variables which are distances r_1 , r_2 , and r_{12} . Possible shapes of the effective potential are shown on Fig. 1. There are four possible cases: (1) minima are asymmetric,

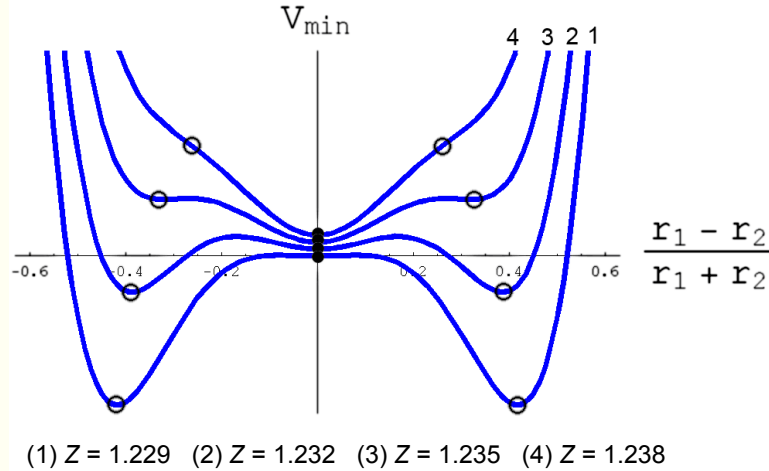


FIG. 1. Shape of the effective potential for helium-like ions in the direction of soft antisymmetric mode. V_{\min} is the minimum of V_{eff} for the given value of the parameter of asymmetry, $\frac{r_1 - r_2}{r_1 + r_2}$. The charge Z is related to the Coulomb force parameter λ as $\lambda = 1/Z$. Curves for different values of Z are shifted along the vertical axis for easier plotting.

(2) minima are asymmetric, with existence of a local symmetric secondary minimum (above the global asymmetric minimum), (3) minimum is symmetric, with two flanking secondary asymmetric minima, (4) a single symmetric minimum, with existence of two asymmetric complex stationary points. A neutral helium atom ($Z = 2$) and all positive ions ($Z \geq 3$) belong to the case (4), with only one symmetric minimum. The particle configuration minimizing the effective potential for helium (the case of $Z = 2$) is shown on Fig. 2.

A. Derivation of large- D limit for two-electron atoms

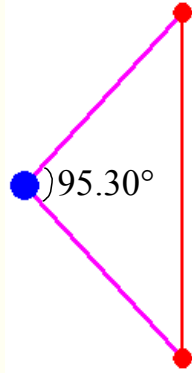


FIG. 2. Configuration minimizing the effective potential for helium atom. The electrons are located in vertices of an isosceles triangle. This fixed-electron configuration is reminiscent of pre-quantum models of Lewis and Langmuire.

(This section is not necessary because in other section derivations are done in a general case of N electrons)

In the earliest paper [13], derivations were based on Holstein-Primakoff representation of a pseudo-spin algebra associated with the Hamiltonian, which is usually done in the method of $1/N$ -expansion in statistical physics. A simpler approach similar to the method described here for harmonic oscillator was adopted in [2, 15?]. This method resembles the analysis of normal modes in the theory of molecular vibrations, and is known as Wilson's GF method. There is another method which may be even simpler because it does not require rescaling of the wavefunction in order to suppress first order derivatives in the Hamiltonian.

Here, we describe the second method based on minimization of the effective potential and studying of normal modes. Expressing Laplacian through derivatives in respect to inter-particle distances according to equation (9),

we obtain

$$\begin{aligned}
T &= -\frac{1}{2} (\nabla_1^2 + \nabla_2^2) \\
&= -\frac{1}{2} \left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + 2 \frac{\partial^2}{\partial r_{12}^2} + 2 \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} + 2 \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} \right. \\
&\quad \left. + \frac{D-1}{r_1} \frac{\partial}{\partial r_1} + \frac{D-1}{r_2} \frac{\partial}{\partial r_2} + 2 \frac{D-1}{r_{12}} \frac{\partial}{\partial r_{12}} \right). \tag{28}
\end{aligned}$$

Here, we use independent variables (r_1, r_2, r_{12}) instead of another variables (r_1, r_2, θ) used in [?], because it allows to avoid transcendental equations during minimization of the potential (containing $\sin \theta$).

The scaling transformation $P = S^{(D-1)/2} \psi$ where

$$S = \frac{1}{4} (2r_1^2 r_{12}^2 + 2r_{12}^2 r_2^2 + 2r_1^2 r_2^2 - r_1^4 - r_2^4 - r_{12}^4)^{1/2} \tag{29}$$

is the area of a triangle with the sides r_1, r_2, r_{12} , removes from equation (28) the terms linear in derivatives. The D -dimensional Schrödinger equation reduces to the form

$$\begin{aligned}
&\left(-\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2} \frac{\partial^2}{\partial r_2^2} - \frac{\partial^2}{\partial r_{12}^2} - \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - \frac{r_2^2 + r_{12}^2 - r_1^2}{r_2 r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} \right. \\
&\left. + V_{\text{eff}}(r_1, r_2, r_{12}) - E \right) P(r_1, r_2, r_{12}) = 0, \tag{30}
\end{aligned}$$

where

$$V_{\text{eff}}(r_1, r_2, r_{12}) = \frac{(D-1)^2}{32} \frac{r_1^2 + r_2^2}{S^2(r_1, r_1, r_{12})} - \frac{1}{r_1} - \frac{1}{r_2} + \frac{\lambda}{r_{12}}. \tag{31}$$

Following derivations are similar to those for harmonic oscillator. First, we make scaling transformation of variables, $r_1 \rightarrow \tilde{r}_1 = D^{1/2} r_1$, $r_2 \rightarrow \tilde{r}_2 = D^{1/2} r_2$, $r_{12} \rightarrow \tilde{r}_{12} = D^{1/2} r_{12}$, and rewrite equation (30) in the form

$$\begin{aligned}
&\left(-\frac{1}{2D^2} \frac{\partial^2}{\partial \tilde{r}_1^2} - \frac{1}{2D^2} \frac{\partial^2}{\partial \tilde{r}_2^2} - \frac{1}{D^2} \frac{\partial^2}{\partial \tilde{r}_{12}^2} - \frac{1}{D^2} \frac{\tilde{r}_1^2 + \tilde{r}_{12}^2 - \tilde{r}_2^2}{\tilde{r}_1 \tilde{r}_{12}} \frac{\partial^2}{\partial \tilde{r}_1 \partial \tilde{r}_{12}} - \frac{1}{D^2} \frac{\tilde{r}_2^2 + \tilde{r}_{12}^2 - \tilde{r}_1^2}{\tilde{r}_2 \tilde{r}_{12}} \frac{\partial^2}{\partial \tilde{r}_2 \partial \tilde{r}_{12}} \right. \\
&\left. + U(\tilde{r}_1, \tilde{r}_2, \tilde{r}_{12}) - \tilde{E} \right) \tilde{P}(\tilde{r}_1, \tilde{r}_2, \tilde{r}_{12}) = 0, \tag{32}
\end{aligned}$$

Then, we determine a minimum of the potential $\tilde{V}_{\text{eff}} = U_0$ (see my old notes). On the next step, we define a function $Y(x, y, z) = \tilde{P}(\tilde{r}_1 + D^{-1/2}x, \tilde{r}_2 + D^{-1/2}y, \tilde{r}_{12} + D^{-1/2}z)$. Next, we define normal-mode coordinates q_1, q_2, q_3 , that simultaneously diagonalize the matrix of second derivatives and the matrix of second-order harmonic terms in the potential ...

...

Coefficients of the $1/D$ -expansion are factorially divergent, $E_k \sim \text{Re}(ca^k) k^\beta k!$.

The ground state has oscillator quantum numbers $(\nu_1, \nu_2, \nu_3) = (0, 0, 0)$. The lowest triplet state has oscillator quantum numbers $(1, 0, 0)$.

Factoring-out the singularity at $D = 1$ could significantly improve the accuracy [9].

VIII. GENERAL CASE OF N -ELECTRON ATOM

There appear several questions that should be addressed in a general case of N electrons.

Finding the global minimum of the effective potential (??) could be intractable problem in case of too many variables. For this reason, the paper [10] is focused on finding the totally symmetric minimum corresponding to a $N - 1$ -dimensional regular hyper-tetrahedron (simplex) configuration of N electrons. The center of the hyper-tetrahedron could be shifted in respect to the nucleus, so the configuration is characterized by only two parameters, the size of the simplex and the shift. These parameters could be determined analytically [10]. It appears that for light atoms with $N < 12$ the situa-

tion with the potential minima is similar to cases (4) or (3) on Fig. 1 for two-electron atoms, when the symmetric minimum is the global minimum. However, for larger N , the global minimum is asymmetric, corresponding to the case (2) for two electron atoms. Nevertheless, the symmetric minimum is located only slightly above the global minima, and it is believed to be a good approximation to the large- D limit.

Assigning certain oscillator quantum numbers is a non-trivial task for a many-electron atom. For atoms starting from lithium, there exist excitations along antisymmetric modes because spinless ground state no longer satisfy Pauli principle (the fact that the wavefunction including spin variables is totally antisymmetric). For this reason, some of oscillator quantum numbers are non-zero, another could be zero. It was shown [10] that with an exception of several light atoms, there are only five different frequencies, one of which has a $(N - 1)$ -fold degeneracy, another has $\frac{1}{2}N(N - 3)$ -fold degeneracy, and other frequencies are non-degenerate. Loeser used the limiting case of $\lambda \rightarrow 0$ (non-interacting electrons) to assign the proper quantum numbers. Details of derivations were published later in [5, 12].

The $(D - 1)$ -scaling procedure proposed by Herschbach [9] should be generalized for electrons on arbitrary shell ($n = 2, 3, \dots$). Loeser used the method of “multiple scaling” described in the next section.

Loeser found that inclusion of the first order correction always worsens the accuracy of $1/D$ -expansion (except of lightest atoms helium and lithium). He proposed an ad hoc method which he called “ $1\frac{1}{2}$ -term approximation” by expanding the first order coefficient E_1 in powers of electron repulsion force parameter $\lambda = 1/Z$ and keeping only the leading-order $1/Z$ -term. He found

that this approximation is the most accurate and he suggested an explanation of this fact based on the divergence of $1/D$ -series.

A. Classical limit for N -electron atom

In the $D \rightarrow \infty$ limit, electrons are localized at the minimum of an effective potential,

$$V_{\text{eff}} = - \sum_{i=1}^N \frac{1}{r_i} + \lambda \sum_{i<j} \frac{1}{r_{ij}} + \frac{1}{8} \sum_{i=1}^N \frac{1}{h_i^2}, \quad (33)$$

where the first term is electron-nucleus interaction, the second term is inter-nucleus interaction, and the third term is the analogue of a centrifugal term. In equation (33), h_i is an altitude in the simplex formed by electrons and the nucleus which is dropped from the vertex where the i -th electron is located. Let us find the minimum of the effective potential under a constraint when all radii r_i are equal and all distances r_{ij} are equal, as it was done in Loeser's paper [10] without giving explicit derivations. In this particular case, electrons are located in vertexes of $N - 1$ -dimensional regular simplex. Let us call *radius* R the distance from any vertex of the regular simplex to its center and *displacement* d the distance from the center of the simplex to the nucleus. Since electrons are equidistant from the nucleus, the space of the regular simplex is orthogonal to the displacement vector, and $r_i = \sqrt{R^2 + d^2}$. From purely geometrical considerations, for a regular simplex one could derive (see Appendix B) that the length of the verge equals to $r_{ij} = \sqrt{\frac{2N}{N-1}}R$. It allows to express the potential through R and d ,

$$V = - \sum_{i=1}^N \frac{1}{r_i} + \lambda \sum_{i<j} \frac{1}{r_{ij}} = - \frac{N}{\sqrt{R^2 + d^2}} + \frac{N^{1/2}(N-1)^{3/2}}{2^{3/2}} \frac{\lambda}{R}. \quad (34)$$

In equation (34), the first term is $N \times \frac{1}{r_i}$ (since all r_i are equal), and the second term is $\frac{N(N-1)}{2} \times \frac{\lambda}{r_{ij}}$ (since all r_{ij} are equal).

In order to find the centrifugal potential, we use the following formula for the altitudes,

$$h_i = N \frac{\mathcal{V}}{\mathcal{S}_i}, \quad (35)$$

where \mathcal{V} is the volume of N -dimensional simplex formed by N electrons and the nucleus, and \mathcal{S}_i is the area of $N - 1$ -dimensional side of this simplex formed by all electrons except i -th and the nucleus. We could express

$$\mathcal{V} = \mathcal{S}d/N, \quad (36)$$

where \mathcal{S} is the volume of $N - 1$ -dimensional simplex formed by electrons. Formulas (35) and (36) are N -dimensional generalization of the area of triangle expressed as a product of length of its side times altitude. From equation (35) we obtain

$$h_i = \frac{\mathcal{S}}{\mathcal{S}_i}d. \quad (37)$$

Ratio $\mathcal{S}/\mathcal{S}_i$ could be calculated from geometrical considerations, see Appendix B,

$$\left(\frac{\mathcal{S}}{\mathcal{S}_i}\right)^2 = \frac{N^2 R^2}{R^2 + (N-1)^2 d^2}. \quad (38)$$

Substituting equations (34) and (38) into equation (33), we obtain

$$V_{\text{eff}} = -\frac{N}{\sqrt{R^2 + d^2}} + \sqrt{N} \left(\frac{N-1}{2}\right)^{3/2} \frac{\lambda}{R} + (N-1)^2 \frac{N^{-1}}{8R^2} + \frac{N^{-1}}{8d^2}. \quad (39)$$

The classical limit is the minimum of (39) in respect to variables R and d .

In order to compare subsequent formulas with derivations of Loeser, we shall use other independent variables (r, γ) instead of (R, d) , where r is the

distance r_i , and γ is cosine of an angle between vectors \mathbf{r}_i and \mathbf{r}_j . Old variables are related to new variables according to formulas

$$\begin{aligned} R &= \left[\frac{N-1}{N} (1-\gamma) \right]^{1/2} r \\ d^2 &= \frac{r^2}{N} (1-\gamma + N\gamma). \end{aligned} \quad (40)$$

After substitution of equation (40) into equation (39) we obtain

$$V_{\text{eff}} = -\frac{N}{r} + \frac{2^{-3/2} \lambda N (N-1)}{\sqrt{1-\gamma}} + \frac{1}{8r^2} \frac{(\gamma(N-2) + 1)N}{(1-\gamma)(\gamma(N-1) + 1)}. \quad (41)$$

Derivatives of the potential (41) in respect to r and γ coincide expressions in Eq. (68) from the paper [12]. The equation for γ is the same as formula (69) from [12],

$$8Z^2\gamma^2 [2 + (N-2)\gamma]^2 + \gamma - 1 = 0, \quad (42)$$

and expressions for r and E are the same as formulas (71) and (72) from [12],

$$\begin{aligned} r &= [1 + (N-1)\gamma]^{-2}, \\ E &= -\frac{1}{2} [1 + (N-1)\gamma]^3 [1 + (N-2)\gamma / (1-\gamma)]. \end{aligned} \quad (43)$$

Formulas from Loeser's paper [10] may be obtained by substitution $\gamma = \xi / (\xi - N)$.

The paper deals only with a totally symmetric minimum, ($r_1 = r_2 = \dots = r_N$, r_{ij} the same for all $i < j$). Let us consider a less symmetric minimum, with $r_1 = r_2 = \dots = r_{N-1}$, $r_{1N} = r_{2N} = \dots = r_{N-1,N}$, and the same r_{ij} for all $i < j \leq N-1$. The energy that was found by minimization of the potential as a function of the parameter $(r_N - r_1) / (r_N + r_1)$ that measures broken symmetry is plotted on Fig. 3. These curves are analogous to multiple-minima curves for two-electron atoms shown on Fig. 1, see also similar plots

in [8], Fig. 5 on p. 26. The asymmetric minimum appears at $Z = 10$, becomes global at $Z = 15$, and turns into almost complete dissociation, $r_N \gg r_1$ for $Z = 50$.

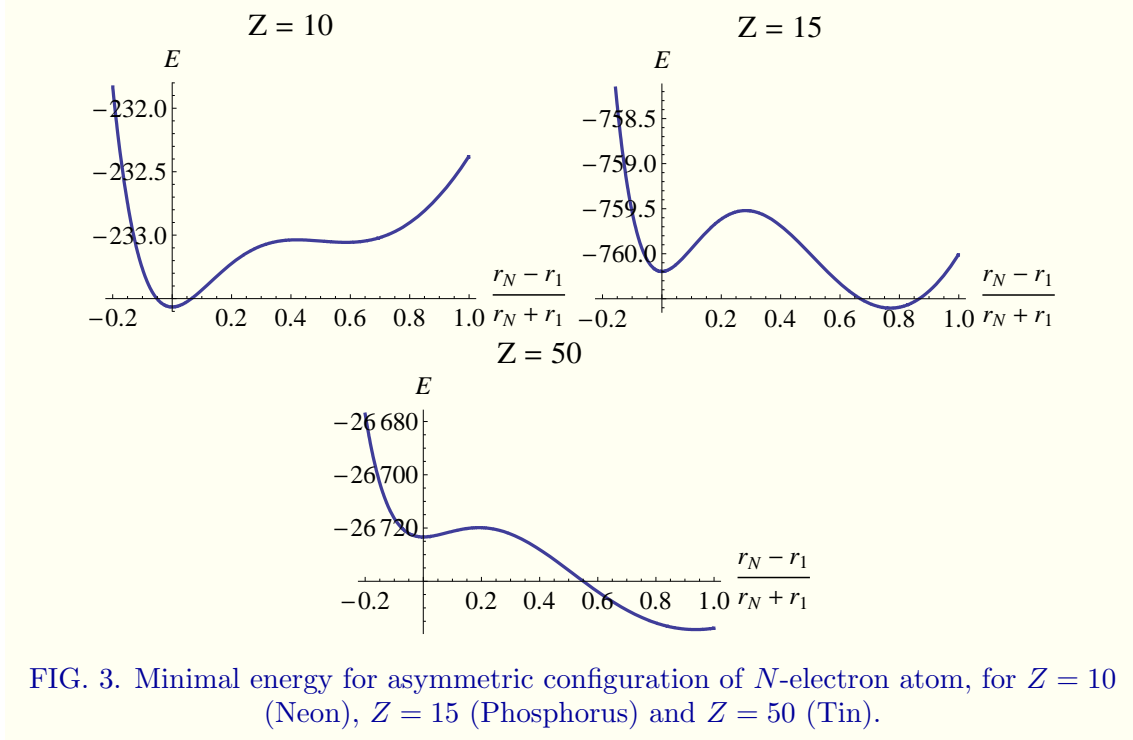


FIG. 3. Minimal energy for asymmetric configuration of N -electron atom, for $Z = 10$ (Neon), $Z = 15$ (Phosphorus) and $Z = 50$ (Tin).

B. Multiple scaling for N -electron atom

Loeser proposed to partition the energy of N -electron atom or an ion with a nuclear charge Z , $E(N, Z)$, into n_{\max} terms, where n_{\max} is the principal quantum number of the outer electron of the atom (within independent-electron filling approximation). Let us call N_n the number of electrons on all shells up to n -th. Then, formally we have

$$E(N, Z) \equiv E(N_{n_{\max}}, Z) = \sum_{n=1}^{n_{\max}} [E(N_n, Z) - E(N_{n-1}, Z)]. \quad (44)$$

In the large- D limit, each term in equation (46) behaves $\sim (2Z/D)^2 [\epsilon_{\infty}(N_n, Z) - \epsilon_{\infty}(N_{n-1}, Z)]$, where $\epsilon_{\infty} = E_0/4$, and E_0 is zero-order

coefficient given by equation (26). If we use unscaled version of the large- D limit, then we have

$$E = \sum_{n=1}^{n_{\max}} \left[\frac{2Z}{D} \right]^2 [\epsilon_{\infty}(N_n, Z) - \epsilon_{\infty}(N_{n-1}, Z)] = \left[\frac{2Z}{D} \right]^2 \epsilon_{\infty}(N, Z). \quad (45)$$

Loeser observed that for large Z when interaction between electrons is relatively small, the energy for each shell is given by Rydberg formula for energy of hydrogen atom in excited state with a principal quantum number n times the number of electrons on this shell. He suggested to replace $\sim (2Z/D)^2$ behavior by an equivalent (in large- D limit) behavior $\sim [2Z/(D + 2n - 3)]^2$. For example, for $n = 1$ we have familiar behavior $\sim (D - 1)^{-2}$ for D -dimensional ground state of a hydrogen atom. The advantage is that in the independent-electron hydrogenic limit of $\lambda = 0$ this behavior is exact, since it represents Rydberg formula for the D -dimensional hydrogen atom. Thus, Loeser's multiple-scaled approximation is given by the following formula (Eq. (16) from his paper [10]),

$$E = \sum_{n=1}^{n_{\max}} \left[\frac{2Z}{D + 2n - 3} \right]^2 [\epsilon_{\infty}(N_n, Z) - \epsilon_{\infty}(N_{n-1}, Z)]. \quad (46)$$

Loeser called this approximation “1-term” because it involves only the leading large- D behavior, without $1/D$ correction that appears from taking into account normal-mode vibrations. He also considered “2-term” approximation that requires a sophisticated assignment of oscillator quantum numbers. He found that “2-term” approximation is always less accurate than “1-term” approximation except for the lightest atom helium, and he explained this fact by divergence of $1/D$ -expansion. In addition, Loeser considered so-called “ $1\frac{1}{2}$ -term” approximation which is the sum of “1-term” and

the large- Z limit of the $1/D$ correction. He found that this approximation appears to be the most accurate.

IX. POSSIBLE GENERALIZATIONS OF LOESER'S MODEL

Recently, there was renewed interest in application of large- D methods for many-electron atoms and molecules [3, 14]. The authors use Bohr-inspired effective potential that resembles the Bohr-like model for helium. For a heuristic derivation of the potential, see [7].

For a given number of electrons N and nuclear charge Z ($Z = N$ for a neutral atom), the effective potential is defined as

$$W = W_1 + W_2, \quad (47)$$

where

$$W_1 = \sum_{i=1}^N \left(\frac{n_i^2}{2r_i^2} - \frac{Z}{r_i} \right), \quad (48)$$

$$W_2 = \sum_{i<j} \frac{1}{r_{ij}}, \quad (49)$$

$$r_i = |\mathbf{r}_i|, \quad r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|. \quad (50)$$

In (48), n_i for $i = 1, 2, 3, \dots, N$ is a principal quantum number of i -th electron.

The energy W is minimized in respect to vectors $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$. This minimization was performed in the original version of the model in 3-dimensional space. Detailed study of geometric configurations and their symmetries was done in [3]. There are three main differences in obtained minimal configurations between large- D limit and Bohr-like model. In large- D limit, the

hyperplane of electronic configuration is always shifted away from the nucleus, to avoid infinity of the centrifugal potential when altitudes in equation (33) go to zero. In contrast, for Bohr-like model the configuration is either co-linear with the nucleus ($N = 2$), co-planar ($N = 3$ or $N = 4$), or three-dimensional ($N \geq 5$). In large- D limit, *all* electrons form a regular simplex, while in Bohr-like model only electrons *on each shell* (the same n_i) form a regular simplex, at least for $N \leq 6$ (for the last case of $N = 6$ the external shell tetrahedron is not perfectly regular). Finally, the dimensionality of the electron-nucleus configuration gradually increases as N in case of large- D limit of N -electron atom, while for Bohr-like model it firstly increases as 1, 1, 2, 2, 3 for $N = 1, 2, 3, 4, 5$, then it stays three-dimensional for $N \geq 5$. Since no regular simplex with more than four vertices exists in three-dimensional space, it is easy to understand that the symmetry of a shell with more than four electrons like $n = 2$ shell for atoms of nitrogen or oxygen is broken. The last fact could be remedied if we allow the electron configuration space to grow beyond $D = 3$ with increase on N , see discussion below.

Bohr energies for large atoms could be lowered by minimizing in coordinate space with more than three dimensions. With increasing of dimensionality, electronic shells became more and more symmetric, until finally at sufficiently large dimensionality they form a regular multidimensional simplex, with all distances between electrons of the same shell and the nucleus equal. Since any $N + 1$ points always lie in N -dimensional subspace, it is evident that increasing the dimensionality beyond N has no effect on the minimization (in fact, the upper value of dimensionality beyond which the minimization

gives the same result is always less than N for $N \geq 2$ because of co-planarity of electrons and the nucleus). For atoms with more than one electron in the outer shells, all simplexes appear to be co-centric with the nucleus and mutually orthogonal, and the energy function could be expressed through M radii of shells, where M is the number of shells. Since the dimensionality of each simplex equals to number of vertexes minus one, the total dimensionality equals to $Z - M$. For example, for neon atom,

$$W = -\frac{39}{2R_1} + \frac{7\sqrt{7}}{R_2} - \frac{80}{R_2} + \frac{1}{R_1^2} + \frac{16}{R_2^2} + \frac{16}{\sqrt{R_1^2 + R_2^2}}, \quad (51)$$

and the total dimensionality is 8. In equation (51), R_1 and R_2 are radii of the first and the second shells. In Loeser's model [10], all electrons are equidistant from the nucleus and from one other. In the present model, two electrons are located at distance R_1 from the nucleus and eight other electrons are located at distance R_2 . Since spaces of the first and the second shells are orthogonal, the distance between electrons on two different shells equals to $\sqrt{R_1^2 + R_2^2}$. Since one could find in total $2 \times 8 = 16$ of these pairs, their interaction gives the term $\frac{16}{\sqrt{R_1^2 + R_2^2}}$ in equation (51). Centrifugal energy for electrons on the first shell equals to $2 \times \frac{1}{2R_1^2}$, and on the second shell $8 \times \frac{2^2}{2R_2^2}$. It represents 5-th and 6-th terms in equation (51). The first term in equation (51) equals to interaction between first two electrons with the nucleus and between themselves, i.e. $-Z/R_1 - Z/R_1 + 1/(2R_1)$ with $Z = 10$ (the distance between electrons equals to $2R_1$ because they are from opposite sides of the nucleus). Third term in equation (51) equals to interaction between eight electrons on the second shell and the nucleus, $8 \times (-Z/R_2)$, and second term equals to interaction energy between electrons of the second

shell, $28 \times 1 / \left(\frac{4}{\sqrt{7}} R_2 \right)$, where $\frac{4}{\sqrt{7}} R_2$ is the distance between vortices of a 7-dimensional simplex.

The maximum number of minimization variables equals to the number of shells for the heaviest element, which is 7.

In the model considered by Loeser[10], all electrons are equivalent. The kinetic energy term is different from our model. Particularly, it turns to infinity if the electrons and the nucleus form a polytope of dimensionality less than Z . It appears that electrons form a regular $Z - 1$ -dimensional simplex, and the nucleus is shifted in direction of Z -th dimension in respect to the center of the simplex. In this case, the electronic configuration is described only by two parameters, R and d , or alternatively by R and θ as in [10]. Unlike Loeser's case, in our model *each shell* forms a regular multidimensional simplex. Our total configuration is a superposition of several simplexes, one simplex for each shell.

Errors of Bohr model in three dimensions and in many dimensions are shown on Fig. 4, juxtaposed on the plot taken from the paper[10]. Bohr model in many dimensions lowers the energy in comparison with 3D-model, and it gives better accuracy 1.5% for large Z , instead of 4.3% for 3D-model. Unlike Loeser's model, our approximation over-estimates energy for small Z and under-estimates it for large Z . Since our approximation is just zero-order classical limit, it does not exhibit unphysical fine structure which arises from changing vibrational state[10].

In a later publication [16], Loeser developed a method of "sub-hamiltonians" which closely resembles our method, where he "boosted" centrifugal potential for each electron by a factor of n^2 . Unlike our method,

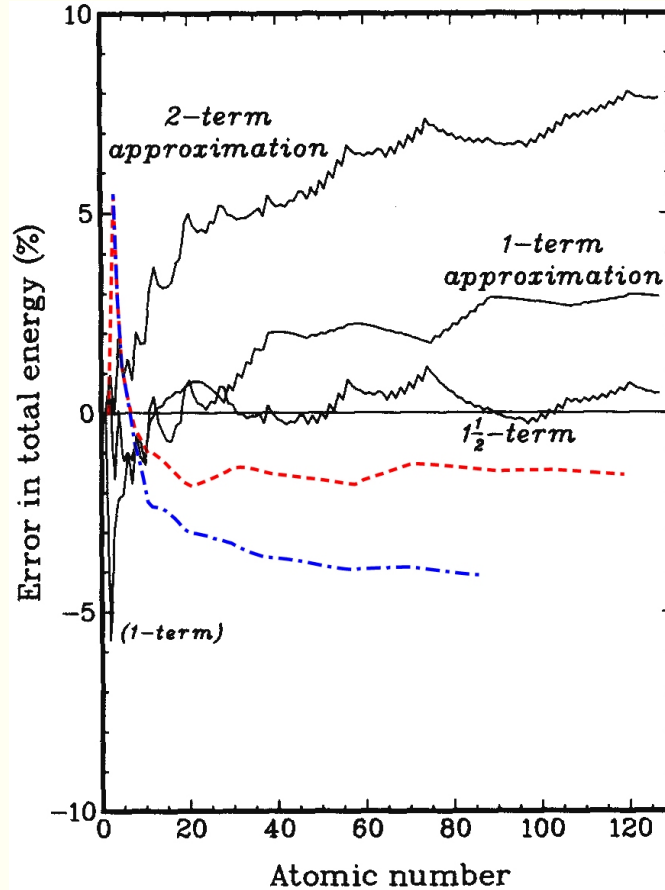


FIG. 4. Accuracy of Bohr model as a function of Z . Solid lines are approximations introduced in [10]. Dot-dashed line are results of the Bohr model based on a minimization of classical configurations in three dimensional space, and dashed line in multidimensional space.

his centrifugal terms include angular dependence. For Z of order of 10, the method under-estimates the energy by around 3%. For very large Z , the error is asymptotically 1.5% which is the same as in our method.

APPENDIX A: VOLUME OF A SIMPLEX AND ITS DERIVATIVES

Here, we derive several formulas necessary for elimination of first-order derivatives and derivation of the effective potential.

We start from a known formula [?] for volume of a simplex with N

vertices represented by vectors $\mathbf{r}_0, \mathbf{r}_1, \dots, \mathbf{r}_N$ in N -dimensional space,

$$V = \pm \frac{1}{n!} \det(\mathbf{r}_1 - \mathbf{r}_0, \mathbf{r}_2 - \mathbf{r}_0, \dots, \mathbf{r}_N - \mathbf{r}_0), \quad (\text{A1})$$

where each column of the $N \times N$ determinant is the corresponding vector difference.

Now, we derive a corollary of equation (A1) which gives in fact a more general formula for the volume in a vector space of *any dimensions*. Defining a matrix $\{S_{i\alpha}\}$ with matrix elements $S_{i\alpha} = (\mathbf{r}_\alpha)_i - (\mathbf{r}_0)_i$, equation (A1) may be rewritten as $V = \pm \frac{1}{n!} \det \mathbf{S}$. Since determinant of a product of two matrices equals to the product of determinants, $V^2 = \frac{1}{n!^2} \det(\mathbf{S}^T \mathbf{S})$, or

$$V^2 = \frac{1}{n!^2} \det \mathbf{Q}, \quad (\text{A2})$$

where \mathbf{Q} is $N \times N$ square matrix whose elements are $Q_{\alpha\beta} = (\mathbf{r}_\alpha - \mathbf{r}_0, \mathbf{r}_\beta - \mathbf{r}_0)$. This formula is valid even in a space with dimensionality more than N because any $N + 1$ vertices always lie in some N -dimensional subspace, where we could prove equation (A2). Since scalar products of vectors in the original space are the same as in N -dimensional subspace, the formula could be applied for vectors in any dimensions.

The formula (A2) could be considered as an expression of the simplex volume through length of its edges, if we express scalar products according to equation (7) as

$$Q_{\alpha\beta} = (\mathbf{r}_\alpha - \mathbf{r}_0, \mathbf{r}_\beta - \mathbf{r}_0) = \frac{1}{2} (r_\alpha^2 + r_\beta^2 - r_{\alpha\beta}^2), \quad (\text{A3})$$

where $r_\alpha \equiv r_{0\alpha} = \sqrt{(\mathbf{r}_\alpha - \mathbf{r}_0)^2}$ and $r_{\alpha\beta} = \sqrt{(\mathbf{r}_\alpha - \mathbf{r}_\beta)^2}$. For example, in the case of $N = 2$ we have Heron's formula for the area of a triangle with sides

r_1 , r_2 , and r_{12} ,

$$V^2 = \frac{1}{16} \begin{vmatrix} 2r_1^2 & r_1^2 + r_2^2 - r_{12}^2 \\ r_2^2 + r_1^2 - r_{12}^2 & 2r_2^2 \end{vmatrix} \quad (\text{A4})$$

$$= \frac{1}{16} (r_1 + r_2 + r_{12})(-r_1 + r_2 + r_{12})(r_1 - r_2 + r_{12})(r_1 + r_2 - r_{12}).$$

Let us calculate a derivative of V^2 in respect to r_α . Using a general formula for a derivative of a determinant, we find

$$\frac{\partial V^2}{\partial r_\alpha} = \sum_{\beta, \gamma} \frac{\partial Q_{\beta\gamma}}{\partial r_\alpha} U_{\beta\gamma}, \quad (\text{A5})$$

where $U_{\beta\gamma}$ is the cofactor of the element $Q_{\beta\gamma}$ in the matrix \mathbf{Q} , i.e. (β, γ) minor times $(-1)^{\beta+\gamma}$. Using the identity

$$\frac{\partial Q_{\beta\gamma}}{\partial r_\alpha} = r_\alpha (\delta_{\alpha\beta} + \delta_{\alpha\gamma}), \quad (\text{A6})$$

we obtain from equation (A5)

$$\begin{aligned} \frac{1}{r_\alpha} \frac{\partial V^2}{\partial r_\alpha} &= \sum_{\beta, \gamma} (\delta_{\alpha\beta} + \delta_{\alpha\gamma}) U_{\beta\gamma} \\ &= \sum_{\gamma} U_{\alpha\gamma} + \sum_{\beta} U_{\alpha\beta} = 2 \sum_{\beta} U_{\alpha\beta}. \end{aligned} \quad (\text{A7})$$

After multiplying equation (A7) by $Q_{\gamma\alpha}$ and summing over α we obtain

$$\begin{aligned} \sum_{\alpha} Q_{\gamma\alpha} \frac{1}{r_\alpha} \frac{\partial V^2}{\partial r_\alpha} &= 2 \sum_{\alpha, \beta} Q_{\gamma\alpha} U_{\alpha\beta} \\ &= 2V^2 \sum_{\beta} \delta_{\gamma, \beta} = 2V^2. \end{aligned} \quad (\text{A8})$$

In derivation of equation (A8), we used a fact that the matrix of cofactors equals to the inverse matrix times the determinant. Using the identity $\partial V^2 / \partial r_\alpha = 2V \partial V / \partial r_\alpha$, we could rewrite equation (A8) in equivalent vector

form as

$$\sum_{\beta} \frac{Q_{\alpha\beta}}{r_{\beta}} \frac{\partial V}{\partial r_{\beta}} = V \quad (\text{A9})$$

It is the final expression that is used during a process of elimination of first-order derivatives in section III.

The derivatives could be in principle found by solving this system of linear equations,

$$\begin{pmatrix} \frac{1}{r_1} \frac{\partial V}{\partial r_1} \\ \frac{1}{r_2} \frac{\partial V}{\partial r_2} \\ \dots \\ \frac{1}{r_N} \frac{\partial V}{\partial r_N} \end{pmatrix} = V \mathbf{Q}^{-1} \begin{pmatrix} 1 \\ 1 \\ \dots \\ 1 \end{pmatrix}. \quad (\text{A10})$$

For derivation of the centrifugal potential, we need another relationship between derivatives,

$$\frac{1}{V} \sum_{\beta \neq \alpha} \frac{1}{r_{\alpha\beta}} \frac{\partial V}{\partial r_{\alpha\beta}} = \frac{1}{h_{\alpha}^2} \quad (\text{A11})$$

for any α , where h_{α} is the length of an altitude dropped from the vertex α to the opposite face of the simplex, i.e. the distance from this vertex to the $N-1$ dimensional plane where the rest of the vertexes lie. Since we could always change enumeration of vertexes of the simplex so that α -th vertex become the 1-st vertex, it is sufficient to prove this identity only for a particular case of $\alpha = 1$. In this case equation (A11) may be rewritten as

$$\frac{1}{V} \left(\frac{1}{r_1} \frac{\partial V}{\partial r_1} + \sum_{\alpha=2}^N \frac{1}{r_{1\alpha}} \frac{\partial V}{\partial r_{1\alpha}} \right) = \frac{1}{h_1^2}. \quad (\text{A12})$$

After multiplying equation (A12) by V^2 , it could be rewritten in an equivalent form

$$\frac{1}{2} \left(\frac{1}{r_1} \frac{\partial V^2}{\partial r_1} + \sum_{\alpha=2}^N \frac{1}{r_{1\alpha}} \frac{\partial V^2}{\partial r_{1\alpha}} \right) = \frac{V^2}{h_1^2}. \quad (\text{A13})$$

Expressing V^2 through a determinant of the matrix \mathbf{Q} , equation (A2), with elements given by equation (A3), we could calculate l.h.s. of equation (A13)

as

$$\frac{1}{2} \sum_{\alpha', \beta'} \left(\frac{1}{r_1} \frac{\partial Q_{\alpha', \beta'}}{\partial r_1} + \sum_{\alpha=2}^N \frac{1}{r_{1\alpha}} \frac{\partial Q_{\alpha', \beta'}}{\partial r_{1\alpha}} \right) U_{\alpha', \beta'}, \quad (\text{A14})$$

where $U_{\alpha', \beta'}$ is a cofactor of the element $Q_{\alpha', \beta'}$. Let us consider three cases. (1) If $\alpha' = \beta' = 1$, then $Q_{\alpha', \beta'} = r_1^2$, the expression in brackets in equation (A14) equals to 2, and the corresponding term in the sum gives U_{11} . Since U_{11} is a determinant of a matrix of size $(N-1) \times (N-1)$ with r_1 removed, it equals to $(N-1)!^2 S_1^2$, where S_1 is $N-1$ -dimensional volume of the simplex with vertexes at points $\mathbf{r}_0, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N$. It may be proved by integration that the volume V equals to the product of S_1 and h_1 divided by N . Thus, this term gives $\frac{V^2}{h_1^2}$ which is the same as r.h.s. of equation (A13). (2) If neither α' nor β' is one, then according to equation (A3), the expression in brackets is zero, and there is no contribution to the sum. (3) If either α' or β' is one, but not both of them, then according to the same formula the derivative $\frac{\partial Q_{\alpha', \beta'}}{\partial r_1}$ is cancelled by one of derivatives in the sum over α , and the result is zero. It concludes the proof that l.h.s. in equation (A13) equals to r.h.s. in the same formula.

Let us rewrite equation (A11) for a particular case of $\alpha = 0$,

$$\frac{1}{V} \sum_{\alpha=1}^N \frac{1}{r_\alpha} \frac{\partial V}{\partial r_\alpha} = \frac{1}{h_0^2} \quad (\text{A15})$$

Now, let us calculate the following sum,

$$S \equiv \sum_{\alpha, \beta=1}^N \frac{Q_{\alpha\beta}}{r_\alpha r_\beta} \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta}. \quad (\text{A16})$$

By differentiating both sides of equation (A9) in respect to r_α , dividing by r_α and summing over α , we obtain

$$S + S_1 + S_2 = S_3. \quad (\text{A17})$$

In equation (A17), S , S_1 , and S_2 are the result of differentiation of a three-term product ($Q_{\alpha\beta}$, $1/r_\beta$, and $\partial V/\partial r_\beta$) in l.h.s. of equation (A9), with S given by equation (A16) and

$$S_1 = \sum_{\alpha,\beta=1}^N \frac{1}{r_\alpha} \frac{\partial Q_{\alpha\beta}}{\partial r_\alpha} \frac{1}{r_\beta} \frac{\partial V}{\partial r_\beta}, \quad (\text{A18})$$

$$S_2 = \sum_{\alpha,\beta=1}^N \frac{1}{r_\alpha} Q_{\alpha\beta} \frac{\partial}{\partial r_\alpha} \left(\frac{1}{r_\beta} \right) \frac{\partial V}{\partial r_\beta}. \quad (\text{A19})$$

In equation (A17), r.h.s. is calculated immediately using equation (A15),

$$S_3 = \sum_{\alpha=1}^N \frac{1}{r_\alpha} \frac{\partial V}{\partial r_\alpha} = \frac{V}{h_0^2}. \quad (\text{A20})$$

The sum S_1 is calculated using equation (A6) and subsequently, equation (A15),

$$S_1 = \sum_{\alpha,\beta=1}^N (\delta_{\alpha\alpha} + \delta_{\alpha\beta}) \frac{1}{r_\beta} \frac{\partial V}{\partial r_\beta} = (N+1) \sum_{\beta=1}^N \frac{1}{r_\beta} \frac{\partial V}{\partial r_\beta} = (N+1) \frac{V}{h_0^2}. \quad (\text{A21})$$

The sum S_2 is calculated using the formula $Q_{\beta\beta} = r_\beta^2$ which follows from equation (A3) and subsequently, equation (A15),

$$S_2 = \sum_{\alpha,\beta=1}^N \frac{1}{r_\alpha} Q_{\alpha\beta} \delta_{\alpha\beta} \left(-\frac{1}{r_\beta^2} \right) \frac{\partial V}{\partial r_\beta} = - \sum_{\beta=1}^N \frac{Q_{\beta\beta}}{r_\beta^3} \frac{\partial V}{\partial r_\beta} = -\frac{V}{h_0^2}. \quad (\text{A22})$$

Finally, expressing S as $S = S_3 - S_1 - S_2$ and using equations (A20) - (A22), we obtain

$$\sum_{\alpha,\beta=1}^N \frac{Q_{\alpha\beta}}{r_\alpha r_\beta} \frac{\partial^2 V}{\partial r_\alpha \partial r_\beta} = (1-N) \frac{V}{h_0^2}. \quad (\text{A23})$$

APPENDIX B: GEOMETRICAL PROPERTIES OF A REGULAR SIMPLEX

Here, we firstly prove that in a regular simplex with N vertices, the ratio between the length of its verge and the distance from the center to any of its vertices equals to $\sqrt{\frac{2N}{N-1}}$. Since all regular simplexes with N vertices are “similar”, i.e. they are congruent to the result of a uniform scaling (enlarging or shrinking) of the other, it is sufficient to prove it for one particular example of a simplex with N vertices. Let us consider so-called “standard N -simplex” [?] in N -dimensional coordinate space, with vertices A_i and its center C defined as points with following coordinates,

$$\begin{aligned}
 A_1 & (1, \quad 0, \quad \dots, \quad 0) \\
 A_2 & (0, \quad 1, \quad \dots, \quad 0) \\
 \dots & \dots \quad \dots \quad \dots \quad \dots \\
 A_N & (0, \quad 0, \quad \dots, \quad 1) \\
 C & (1/N, 1/N, \dots, 1/N)
 \end{aligned} \tag{B1}$$

Then, it is straightforward to calculate $|A_i A_j| = \sqrt{2}$ ($i \neq j$) and $|C A_i| = \sqrt{(1 - \frac{1}{N})^2 + \frac{N-1}{N^2}} = \sqrt{\frac{N-1}{N}}$ from which we find that $\frac{|A_i A_j|}{|C A_i|} = \sqrt{\frac{2N}{N-1}}$.

Let us consider a point P at distance d from the center of the regular simplex and equidistant from all of its vertices. We are going to prove that the ratio of the volume of a simplex in which one of points A_i is replaced by P to the volume of the regular simplex $A_1 A_2 \dots A_n$ equals to

$$\frac{S_i}{S} = \sqrt{\frac{R^2 + (N-1)^2 d^2}{N^2 R^2}}. \tag{B2}$$

To prove (B2), we consider a configuration obtained from (B1) by scaling by

a factor of $\sqrt{\frac{N}{N-1}}$,

$$\begin{aligned}
A_1 &: \left(\sqrt{\frac{N}{N-1}}R, \quad 0, \quad \dots, \quad 0 \right) \\
A_2 &: \left(0, \quad \sqrt{\frac{N}{N-1}}R, \quad \dots, \quad 0 \right) \\
&\dots \quad \dots \quad \dots \quad \dots \quad \dots \\
A_N &: \left(0, \quad 0, \quad \dots, \quad \sqrt{\frac{N}{N-1}}R \right) \\
C &: \left(\frac{R}{\sqrt{N(N-1)}}, \quad \frac{R}{\sqrt{N(N-1)}}, \quad \dots, \quad \frac{R}{\sqrt{N(N-1)}} \right)
\end{aligned} \tag{B3}$$

For this scaled simplex, $|CA_i| = R$. Let us consider a point P with coordinates

$$P : \left(\frac{R - \sqrt{N-1}d}{\sqrt{N(N-1)}}, \quad \frac{R - \sqrt{N-1}d}{\sqrt{N(N-1)}}, \quad \dots, \quad \frac{R - \sqrt{N-1}d}{\sqrt{N(N-1)}} \right), \tag{B4}$$

so that $|CP| = d$.

We shall prove (B2) for $i = N$. Let us define a point C_N as a center of the regular simplex $A_1A_2\dots A_{N-1}$,

$$C_N : \left(\frac{N^{1/2}}{(N-1)^{3/2}}R, \quad \frac{N^{1/2}}{(N-1)^{3/2}}R, \quad \dots, \quad \frac{N^{1/2}}{(N-1)^{3/2}}R, 0 \right). \tag{B5}$$

Since the simplexes $A_1A_2\dots A_{N-1}A_N$ and $A_1A_2\dots A_{N-1}P$ have a common base which is a regular simplex $A_1A_2\dots A_{N-1}$, the ratio of their volumes equal to the ratio of their altitudes, $|A_NC_N|/|PC_N|$. Using coordinates of points A_N , C_N , and P given by equations (B3), (B5), and (B4), we find that

$$\begin{aligned}
|A_NC_N|^2 &= (N-1) \frac{N}{(N-1)^3} R^2 + \frac{N}{N-1} R^2 = \frac{N^2}{(N-1)^2} R^2 \\
|PC_N|^2 &= (N-1) \left(\frac{R - \sqrt{N-1}d}{\sqrt{N(N-1)}} - \frac{N^{1/2}}{(N-1)^{3/2}}R \right)^2 + \left(\frac{R - \sqrt{N-1}d}{\sqrt{N(N-1)}} \right)^2 \\
&= \frac{R^2}{(N-1)^2} + d^2,
\end{aligned} \tag{B6}$$

Since $\mathcal{S}^2/\mathcal{S}_N^2 = |PC_N|^2/|A_N C_N|^2$, we could find the formula (38) using equation (B6).

-
- [1] J. Avery, D. Z. Goodson, and D. R. Herschbach, *Dimensional scaling and the quantum mechanical many-body problem*, *Theor. Chim. Acta* **81** (1991), 1–20.
- [2] A. A. Belov, Y. E. Lozovik, and A. Gonzalez, *Electron clusters in a quadratic potential*, *Physics Letters A* **142** (1989), 389–392.
- [3] G. Chen, Z. Ding, S.-B. Hsu, M. Kim, and J. Zhou, *Mathematical analysis of a Bohr atom model*, *Journal of Mathematical Physics* **47** (2006), no. 2, 022107–+.
- [4] M. Dunn, T. C. Germann, D. Z. Goodson, C. A. Traynor, J. D. Morgan, III, D. K. Watson, and D. R. Herschbach, *A linear algebraic method for exact computation of the coefficients of the $1/D$ expansion of the Schrödinger equation*, *J. Chem. Phys.* **101** (1994), 5987–6004.
- [5] M. Dunn, D. K. Watson, and J. G. Loeser, *Analytic, group-theoretic wave functions for confined, correlated N -body systems with general two-body interactions*, *Annals of Physics* **321** (2006), 1939–1980.
- [6] A. Gonzalez and D. Leal, *Binding and excitation energies of Lennard-Jones clusters in the $1/d$ -method*, *Journal of Physics B Atomic Molecular Physics* **26** (1993), 1253–1261.
- [7] R. D. Harcourt, H. Solomon, J. Bechworth, and L. Chislett, *Bohr orbit model and Ruedenberg’s theory of the origin of the binding energy for H_2* , *American Journal of Physics* **50** (1982), 557–559.
- [8] D. R. Herschbach, *Dimensional Scaling in Chemical Physics* (D. R. Herschbach, J. Avery, and O. Goscinski, eds.), Kluwer Academic, Dordrecht, 1993, p. 7.
- [9] ———, *Dimensional scaling and renormalization*, *Int. J. Quant. Chem.* **57** (1998), 295–308.
- [10] J. G. Loeser, *Atomic energies from the large-dimension limit*, *J. Chem. Phys.* **86** (1987), 5635–5646.
- [11] M. López-Cabrera, A. L. Tan, and J. G. Loeser, *Scaling and interpolation for dimensionally generalized electronic structure*, *J. Phys. Chem.* **97** (1993), 24672478.
- [12] B. A. McKinney, M. Dunn, D. K. Watson, and J. G. Loeser, *N identical particles under quantum confinement: a many-body dimensional perturbation theory approach*, *Annals of Physics*

- 310** (2004), 56–94.
- [13] L. D. Mlodinow and N. Papanicolaou, *Pseudo-spin structure and large N expansion for a class of generalized helium Hamiltonians*, *Annals of Physics* **131** (1981), 1–35.
- [14] A. Svidzinsky, G. Chen, S. Chin, M. Kim, D. Ma, R. Murawski, A. Sergeev, M. Scully, and D. Herschbach, *Bohr model and dimensional scaling analysis of atoms and molecules*, *Intern. Rev. Phys. Chem.* **27** (2008), 665–723.
- [15] P. D. T. van der Merwe, *Semiclassical theory of the helium atomic spectrum*, *J. Chem. Phys.* **81** (1984), 5976–5985.
- [16] Z. Zhen and J. Loeser, *Dimensional Scaling in Chemical Physics* (D. R. Herschbach, J. Avery, and O. Goscinski, eds.), Kluwer Academic, Dordrecht, 1993, p. 83.