Scaling relations for the ground-state energies of three-particle systems with Coulomb interaction

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A general approximate expression for the nonrelativistic ground-state energies of Coulomb systems with charges $Z_a = Z_b = \pm 1$ and $Z_c = \mp 1$ and arbitrary masses m_a, m_b, and m_c is suggested. The results obtained with use of this expression are in excellent agreement with precise variational and adiabatic calculations of three-particle electron, muon, and excitonic molecular systems and can be used for the prediction of ground-state energies of yet-untested systems.

The development of computers in recent years had made it possible to transform a variety of methods of quantum mechanics and quantum chemistry into respective numerical algorithms. As a consequence, we now have very precise calculations of more or less simple standard systems. This also opens up new possibilities to treat extremely complicated systems with tens and hundreds of atoms.

Besides enormous successes in the framework of this numerical approach, one negative, tendency can be noticed: very often problems are solved by use of "brute force," which finally leads to competition, the results of which are crucially influenced by the technical characteristics of the computing machines. In a constant struggle with numerical mistakes and instabilities, very little time remains for thinking about the physical picture of the problem and developing the intuition which can lead to a substantial simplification in the solving of these complicated problems.

Numerical calculations are always approximate. Anyone who has developed some complicated numerical program for treating many-particle systems knows how important exact relations which follow from quantum mechanics are for checking the accuracy. A very interesting review of the possibilities for obtaining such exact relations in the quantum theory of atoms and molecules can be found in the recent monograph by Rebane and Penkina.[1] This monograph is devoted to the investigation of regularities which result from the scaling transformation of coordinates and, connected with it, the virial theorem. The book treats the regularities which originate from the Hellmann-Feynman theorem and also the variational principle of quantum mechanics.

All atoms and molecules represent systems of particles interacting via Coulomb interactions which are characterized by a certain assembly of values of masses, charges, and coordinates. This refers not only to ordinary atoms and molecules consisting of electrons and nuclei, but also for their analogous systems formed of electrons and holes in semiconductors, different exotic atomic and molecular systems which includes muons, positrons, nuclei of antimatter, etc. All Coloumbic systems with a fixed number of particles N are similar in the sense that their Hamiltonians transform into each other with appropriate changes of masses and charges, which can be treated mathematically as continuous variables.

The important ingredient of the relations obtained in Ref. 13 is that they do not contain wave functions. These relations connect directly measurable quantities of similar quantum systems.

In the present work we shall mainly be concerned with energetic characteristics of the simplest three-particle atomic and molecular systems. The problem of three particles interacting via the Coulomb interaction is the classical quantum-mechanical problem, which up to now has been the focus of interest of many researchers. This problem appears in different fields of physics (see, for instance, review articles in Ref. 2). Most of the results obtained by solving the three-particle Coulomb problem can be applied to the investigation of other three-particle interactions and to the more complicated many-particle system.

We start with the general many-particle Hamiltonian in the form

$$H(\mathbf{x};\lambda) = T(\mathbf{x}) + V(\mathbf{x}) + \lambda W(\mathbf{x}) , \tag{1}$$

where $\mathbf{x}$ denotes the total set of all particle coordinates. Its normalized eigenfunction $\Psi(\mathbf{x};\lambda)$ and ground-state energy eigenvalue $E(\lambda)$ depend on the real parameter λ. The operators T, V, and W are homogeneous functions of coordinates with the orders of homogeneity $-z$, $-p$, and $-q$, respectively. One of the first attempts to find boundaries for the ground-state energies of atomic and molecular systems can be found in the papers in Ref. 3.

If the conditions $q = z$ or $q = p$ are fulfilled, then a scaling transformation of coordinates gives the following unequalities (cf. Ref. 1, p. 160):

$$f_{pq}(\lambda) \gtrless \frac{(\lambda_a - \lambda) f_{pq}(\lambda_b) + (\lambda - \lambda_b) f_{pq}(\lambda_a)}{\lambda_a - \lambda_b} , \tag{2a}$$

where the upper sign is chosen when $\lambda \in [\lambda_a, \lambda_b]$, while the lower sign is taken for λ out of this interval, and

$$f_{pq}(\lambda) \equiv \mathrm{sgn}(q^2 - 2p) \, | E(\lambda) |^{(2p - q^2)/2p} . \tag{2b}$$

The values λ_a and λ_b are boundaries which are defined by the values of λ for standard systems.

Certain examples of the application of relation (2) are given in Ref. 1 where, on the basis of the known ground-

state energies of standard systems, the limits for energies of similar systems were obtained by means of changing masses or charges of particles. We shall treat only three particles interacting via the Coulomb interaction. The Hamiltonian of three charged particles, with the center-of-mass motion excluded, has the form

$$H(\mathbf{r},\mathbf{R})=-\frac{1}{2}\frac{m_a+m_b}{m_a m_b}\Delta_{\mathbf{R}}-\frac{1}{2}\left[\frac{1}{4m_a}+\frac{1}{4m_b}+\frac{1}{m_c}\right]\Delta_{\mathbf{r}}$$
$$-\frac{1}{4}\left[\frac{1}{m_a}-\frac{1}{m_b}\right](\nabla_{\mathbf{R}}\cdot\nabla_{\mathbf{r}}+\nabla_{\mathbf{r}}\cdot\nabla_{\mathbf{R}})$$
$$+\frac{Z_aZ_b}{|\mathbf{R}|}+\frac{Z_aZ_c}{|\mathbf{r}+\mathbf{R}/2|}+\frac{Z_bZ_c}{|\mathbf{r}-\mathbf{R}/2|}\ , \qquad (3)$$

where m_α, Z_α ($\alpha\equiv a$, b, or c) are the masses and charges of three particles, and the respective coordinates are given in Fig. 1.

In recent years a considerable number of papers have appeared which have been devoted to the nonadiabatic calculations of the ground and excited states of such three-particle systems. Very precise ground-state energies of these systems have been obtained with great effort by means of the variational method,[4] as well as by the perturbed-stationary-states (PSS) method.[2(a)] In these methods a large number of different types of matrix elements is needed and complicated numerical programs must be developed.

The general formula (2) for the ground-state energy limits can be relatively successful only in the case $m_a=m_b\neq m_c$ (cf. Ref. 1, p. 165). It has to be noted that the limits for the ground-state energies become crude in the case of considerable changes in the ratios of particle masses.

With this fact in mind, the direct-interpolation procedures become interesting. One of the attempts, which uses the scaling transformation of coordinates and the expansion of energy in powers of the Born-Oppenheimer parameter, made it possible to derive the formula for the ground-state energy of the three-particle Coulomb symmetric systems ($m_a=m_b=m$).[5] In that case the Hamiltonian (3) takes the form

$$H=m\beta\hat{h}(\mathbf{s},\mathbf{t};\beta)\ . \qquad (4)$$

Here $\beta=m_c/(2m+m_c)$, $\mathbf{s}$ and $\mathbf{t}$ are scaled coordinates

$$\mathbf{s}=-m\beta\mathbf{R},\quad \mathbf{t}=-2m\beta\mathbf{r}\ ,$$

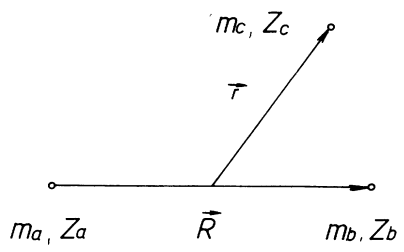

FIG. 1. Coordinate system for three particles a, b, and c. The origin of vector $\mathbf{r}$ is in the middle of the vector $\mathbf{R}$.

while $\hat{h}$ is given by

$$\hat{h}=-\beta\Delta_{\mathbf{s}}-\Delta_{\mathbf{t}}+\frac{Z_aZ_b}{|\mathbf{s}|}+\frac{2Z_aZ_c}{|\mathbf{t}+\mathbf{s}|}+\frac{2Z_bZ_c}{|\mathbf{t}-\mathbf{s}|}\ . \qquad (5)$$

Let ϵ be the lowest eigenvalue of the operator (5). This value is connected with the ground-state energy of the system described by the Hamiltonian (4) by the obvious relation

$$E(m,m,m_c)=m\beta\epsilon(\beta)\ . \qquad (6)$$

The function $\epsilon(\beta)$ is defined in the interval $0\leq\beta\leq 1$. The knowledge of this function makes it possible to find the ground-state energies of all Coulomb systems with masses $m_a=m_b=m$ and m_c and charges Z_a, Z_b, and Z_c.

In Ref. 5 the following approximate expansion of the function ϵ in powers of the Born-Oppenheimer parameter $\beta^{1/4}$ was suggested:

$$\epsilon(\beta)\approx f(\beta)=\sum_{j=0}^{5}c_j\cdot\beta^{j/2}\ . \qquad (7)$$

Unknown coefficients were determined on the basis of the very precisely known ground-state energies of six standard systems. The standard systems were chosen to make the interval of variations of β as wide as possible. The details of the fitting procedure and the standard systems which had been used can be found in Ref. 5. Here, we give only the values of the coefficients:

$$C_0=-1.205\,268\,43,\quad C_1=0.641\,664\,62\ ,$$
$$C_2=0.288\,839\,86,\quad C_3=-0.170\,338\,48\ ,$$
$$C_4=-0.199\,739\,85,\quad C_5=0.117\,091\,27\ .$$

The formula (6) is obtained without any assumptions about the adiabatic separation of variables, so it is valid for the true nonrelativistic energies of three-particle systems. But the choice of the standard systems in Ref. 5 limited the application of the formula (7) only to the cases where $Z_a=Z_b=\pm 1$, $Z_c=\mp 1$, and $m_a=m_b=m$.

Many interesting muonic, excitonic, etc., systems, with $m_a\neq m_b$ are beyond the scope of formulas (6) and (7) and all attempts to scale their ground-state energies have been unsuccessful.

We have attempted to find some analytical scaling relations which connect total ground-state energies of these systems. After many unsuccessful attempts, we realized that, with a remarkable exactness, the following simple empirical formula can be used ($Z_a=Z_b=\pm 1$, $Z_c=\mp 1$):

$$E(m_a,m_b,m_c)=\tfrac{1}{2}[E(m_a,m_a,m_c)+E(m_b,m_b,m_c)]\ . \qquad (8)$$

The results obtained using this formula for the energies of some molecular and mesomolecular systems are given in Table I.

The accuracy of the results given in the Table I is extremely good, bearing in mind the differences between the results obtained with much more complicated and laborous methods [cf. Tables 4 and 5 from Ref. 2(a)].

In conclusion, we want to emphasize that it is now possible to obtain nonrelativistic ground-state energies of all three-particle Coulomb systems very easily and precisely

TABLE I. Total molecular ground-state energy E obtained using formulas (7) and (8). E_{var} represent results of variational calculations of the same quantity (these results are almost the same as PSS results[2(a)]).

Molecule	$E_{1/2}$ (eV)	E_{var} (eV)	$(E_{1/2}-E_{\text{var}})/E^{\text{var}}$
$pd\mu$	−2884.70	−2884.4219	1.55×10^{-5}
$pt\mu$	−2927.675	−2924.1816	1.19×10^{-3}
$dt\mu$	−3031.055	−3029.2516	5.95×10^{-4}
pde	−16.271 017	−16.269 258	1.08×10^{-4}

[formulas (6), (7), and (8)]. For the time being, the only limitation is $Z_a=Z_b=\pm1$, $Z_c=\mp1$. At first sight, this looks like a very sharp limitation. But a large number of excitonic systems in a variety of semiconductors can be treated by our method.

As an illustration, we shall present the calculation of the ground-state energy of the exciton ionized-donor complex in the CdS I system. This system was investigated experimentally, as well as theoretically.[6]

The fundamental constants of CdS I are[6,7] $m_e^*=0.18$, $\sigma=m_e^*/m_h^*=0.182$ (masses are given in units of the electron mass m_e). The values of the dielectric constants for an atom consisting of an electron and an ionized donor, and for an excitonic atom are $K_D=9.031$ and $K_x=8.7578$, respectively.

Applying the formula (6) to the symmetric systems consisting of two ionized donors and the electron with the effective mass m_e^* we obtain

$$E(\infty,\infty,m_e^*)=\tfrac{1}{2}\epsilon(\beta)\left[\frac{m_e^*e^4}{\hbar^2K_D^2}\right]=-36.910\,474\ \text{meV}\ .$$

The same expression applied to the system consisting of two holes and one electron gives

$$E(m_h^*,m_h^*,m_e^*)\equiv\frac{1}{2+\sigma}\epsilon(\beta)\left[\frac{m_e^*e^4}{\hbar^2K_x^2}\right]$$

$$=-29.298\,662\ \text{meV}\ .$$

According to our formula (8), one can easily get

$$E(\infty,m_h^*;m_e^*)=-32.744\,568\ \text{meV}\ .$$

This value is to be compared with the experimental total energy of this system, which is equal to $E^{\text{expt}}=-33.62$ meV, and the theoretical value, obtained by means of much more complicated anisotropic variational calculations, $E^{\text{calc}}=-30.970\,1197$ meV.[6]

Our result is in much better agreement with the experiment ($|\Delta E|/E^{\text{expt}}=2.6\%$) than the variational value ($|\Delta E^{\text{calc}}|/E^{\text{expt}}=7.9\%$). This example, together with Table I, shows the obvious advantage of the method suggested in this work. Although our method is a very simple and empirical one (for the time being), its predicting power is surprising and it gives excellent results in all examples we tested. We can imagine an even more exact empirical formula with the inclusion of the dependence of the difference between masses m_a and m_b in the formula (8),

$$E(m_a,m_b,m_c)=\alpha(m_a-m_b)E(m_a,m_a,m_c)+\gamma(m_a-m_b)E(m_b,m_b,m_c)\ ,$$

but the simplicity and the exactness of formula (8) is sufficiently good in our opinion.

The difference between the experimental total energy of the three-particle excitonic systems and the value obtained from our formula (8) can be used for the estimation of the anisotropy of effective masses of electrons and holes in semiconductors. We hope that similar scaling relations can be found for other types of interactions.

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