DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ANL/PHY/CP - 8/870
Conf-931252--1

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

NONLINEARITY AS AN ORIGIN OF NONUNIQUENESS IN SOLUTION OF HARTREE'S EQUATION

M. Ya. Amusia

Argonne National Laboratory, Physics Division, Argonne, IL 60439, USA

and

A. F. Ioffe Physical - Technical Institute, St. Petersburg, 194021 RUSSIA

FEB 16 1984
OSTI

There is almost no doubt, that the surrounding macroscopical world, its chemistry and biology is described by the Schrodinger equation, which includes all particles and their interaction. In a very large scale of distances the interaction is of electromagnetic nature and can be presented as a sum of potential energies of all pairs of particles. The solution of the Schrodinger equation gives the wave function of any considered system and via it all observable characteristics can be calculated, in principle.

The Schrodinger equation is linear so it has unique solutions. However containing coordinates and momenta of all particles of the system, it is almost unsolvable for really macroscopical objects and must be simplified. One of the most important steps in this direction was made by Hartree in the twenties [1], leading to nonlinear equations which bear his name. These equations are very widely used in modern physics in calculating the ground and excited states of atoms, molecules, nuclei, and solids. They are nonlinear and therefore may have solutions with very unusual properties, including lack of uniqueness. Still they are complicated enough and can not be solved for any arbitrary interparticle interaction analytically and thus analyzed.

Here simple models for this interaction are used to show that Hartree's equations can be not single-valued. In the latter case one has a problem as to which of the solutions is closest to the exact wave function for the corresponding Schrodinger equation. Before discussing the models, one must define what is meant by nonuniqueness in solutions.

The wave function of a multielectron system is approximated in Hartree's method by the product of one-particle wave functions, which are selected in a definite fashion. For example, in calculating the ground state of an inert gas it is usual to select the one-particle functions as products of spin (inner electron degree of freedom), angular and radial functions. The latter must satisfy certain boundary conditions. The number of zeros is directly related to the so called principal quantum number. In the case of linear equations, the boundary conditions define the solution quite uniquely. The situation is different for Hartree's equations, as shown below: there may be cases where various radial functions have the given number of nodes and satisfy the equations and boundary conditions.

We consider a system of N identical Fermi-particles moving in the Coulomb attractive field of a nucleus of charge Z and interacting one with another via the pair potential $V(r_1, r_2)$, where $\vec{r}_1$ and $\vec{r}_2$ are the radius vectors of the particles. The

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

g7D

Hamiltonian for such a system (with the electron charge e , its mass m and Planck constant $\hbar$ equal to one, $e = \hbar = m = 1$) is

$$H = -\sum_{i=1}^N \frac{\Delta_i}{2} - \sum_{i=1}^N \frac{Z}{r_i} + \frac{1}{2} \sum_{i \neq k=1}^N V(r_i, r_k). \quad (1)$$

The corresponding Hartree equations take the form

$$\left(-\frac{\Delta}{2} - \frac{Z}{r} + \sum_{i \neq k=1}^N \int dr' |\phi_i(r')|^2 V(r', r) \right) \phi_k(r) = \epsilon_k \phi_k(r). \quad (2)$$

The summation in (2) is extended to all filled states. The total energy E of the system is defined by

$$E = \sum_{k=1}^N \epsilon_k - \frac{1}{2} \sum_{i \neq k=1}^N V_{ik, ik} \quad (3)$$

We now choose a model potential $V(r_1, r_2)$ such that Hartree's equations can be solved analytically.

Consider a potential of the form

$$V(r_1, r_2) = \alpha r_1^{-1} r_2^{-1}, \quad (4)$$

instead of the usual Coulomb one

$$V(r_1, r_2) = |\vec{r}_1 - \vec{r}_2|^{-1}. \quad (5)$$

In (4) α is a constant and is considered positive. We assume that the potential of (4) describes the interaction of the electrons that fill a subshell with the quantum numbers n and ℓ in the atom. Let half of these electrons be described by the wave function $\phi_1(r)$, and the other half by $\phi_2(r)$. Then from (2) and (4) we have

$$\left(-\frac{\Delta}{2} - \frac{Z_{ef}^{(p)}}{r} \right) \phi_p(r) = \epsilon_p(r), \quad (6)$$

$$Z_{ef}^{(p)} = Z - \alpha \sum_{i \neq k=1}^N \int dr' |\phi_i(r')|^2 r'^{-1}. \quad (7)$$

Equation (6) is satisfied by the ordinary wave function for the Coulomb field of the charge $Z_{ef}^{(k)}$. We calculate the integral in (7) to find a system of equations for $Z_{ef}^{(p)}$:

$$Z_{ef}^{(p)} = Z - \frac{\alpha}{n^2} (2\ell Z_{ef}^{(p)} + (2\ell + 1) Z_{ef}^{(q)}). \quad (8)$$

Here $p, q=1, 2$ and $p \neq q$. These equations have the obvious solution

$$Z_{ef}^{(1)} = Z_{ef}^{(2)} = Z \left(1 + \frac{\alpha}{n^2} (4\ell + 1) \right)^{-1}, \quad (9)$$

which will be called normal. If the constant α satisfies the condition $\alpha = n^2$, then system (8) degenerates into a single equation

$$\sum_{p=1,2} (2\ell + 1) Z_{ef}^{(p)} = Z, \quad (10)$$

that has an infinite set of solutions for which $Z_{ef}^{(1)} \neq Z_{ef}^{(2)}, Z_{ef}^{(1)}, Z_{ef}^{(2)} > 0$. These solutions will be called singular. The radial wave functions and one-particle energies of all the electrons in subshell $n\ell$ are identical for the normal solution. For a singular solution, the one-particle energies and the wave functions $\phi_1(r)$ and $\phi_2(r)$ are different. From (3) we find the total energy of the system

$$E = -\frac{Z^2 N}{2n^2} \left(1 + \frac{\alpha}{n^2} (N-1) \right)^{-1}, \quad (11)$$

which coincides for the normal solution and all the singular ones. In deriving (11) it was taken into account that $N=(4\ell+2)$.

Note that at the point of instability, i.e. at $\alpha = n^2$ the total energy E reduces to that of a single particle in the coulomb field of the nucleus with the charge Z :

$$E = -Z^2 / 2n^2, \quad (12)$$

and is N - independent. With increase of α from 0 to n^2 the mean radius R of the system under consideration is growing smoothly, but at $\alpha = n^2$ becomes nondetermined being able to have any value, even $R \rightarrow \infty$. Sets of solutions with $Z^{(1)} \neq Z^{(2)}$ have the same principal quantum number, namely n . So, contrary to the case of linear Schrodinger equation, n is unable to determine uniquely the solution of Hartree nonlinear equation.

The singular solution occurs at a definite strength for interparticle interaction. One solution may go over to the other in a continuous fashion as the parameter approaches the critical value, the energy being preserved, while the size can be arbitrary.

Note, that at $\alpha=n^2$ the energy required to eliminate a particle is according to (12), equal to zero, while the Hartree energy of a particle is nonzero and is almost arbitrary. This difference is a direct manifestation of essential rearrangement of Hartree states after eliminating a particle off the considered system.

The existence of a singular solutions seem to be a reasonable general feature of Hartree equations and is independent of the particular form of the particle interaction. In the above model, the occurrence of singular solutions was not related to any special feature of the shape of the potential well, but solutions arise only from the non-linearity of the equations.

Indeed, we can consider a Hamiltonian, different from (1):

$$H = -\sum_{i=1}^N \frac{\Delta_i}{2} + \sum_{i=1}^N \frac{1}{2} \omega^2 r_i^2 + \frac{1}{2} \sum_{i \neq k=1}^N V(r_i, r_k), \quad (13)$$

which describes N particles moving in a so-called oscillator potential and interacting each other via $V(r_i, r_k)$,

$$V(r_1, r_2) = -\beta r_1^2 r_2^2. \quad (14)$$

Then instead of (6) and (7) one gets

$$\left(-\frac{\Delta}{2} + \frac{1}{2} (\omega_{ef}^{(k)})^2 r^2 \right) \phi_k(r) = \varepsilon_k \phi_k(r), \quad (15)$$

$$(\omega_{ef}^{(k)})^2 = \omega^2 - \beta \sum_{i \neq k=1}^N \int d\vec{r}' |\phi_i(\vec{r}')|^2 r'^2. \quad (16)$$

The solutions of (15) are known and the integrals in (16) may be calculated in a closed form. Separating all the N particles into two groups, as it was done above in deriving (6) and (7), a system of two equations is obtained, which may be semischematically presented as

$$(\omega_{ef}^{(p)})^2 = \omega^2 - \tilde{\beta} (\omega_{ef}^{(q)})^2, \quad p \neq q = 1, 2 \quad (17)$$

where $\tilde{\beta}$ differs from β by a factor, dependent upon the principal quantum number n of the state, occupied by all N particles as well as upon the number of particles in the group 1 and 2, N_1 and N_2 respectively. They are related to N by equation $N=N_1+N_2$.

The system of equations (17) has an obvious solution

$$(\omega_{ef}^{(1)})^2 = (\omega_{ef}^{(2)})^2 = \omega^2 (1 + \tilde{\beta})^{-1}, \quad (18)$$

which is a normal one. However for $\tilde{\beta}=1$ the system (17) becomes degenerate and have an infinite number of solutions, the singular ones, satisfying the equation

$$(\omega_{\alpha}^{(1)})^2 + (\omega_{\alpha}^{(2)})^2 = \omega^2. \quad (19)$$

As in the first example, the corresponding states can be arbitrary stretched in space by choosing one of the frequencies, $\omega_{\alpha}^{(1)}$ or $\omega_{\alpha}^{(2)}$, sufficiently small.

Another, rather interesting example of a Coulomb field Hamiltonian with two-body interactions $\gamma/r_1^2 r_2^2$ was discussed in [2]. It was demonstrated there that starting from some value of γ two instead of one solutions appear.

Traces of the nonuniqueness described above with two instead of one solutions were observed in numerical calculation of Hartree-Fock states for some atoms [3], where however the role of nonlinearity was not clarified [5].

It is natural to examine the relationship between these solutions and the exact solution to the Schrodinger equation with a particle interaction potential (4) or (14). Before this question can be answered, it is necessary to examine the stability of the solutions, which can be easily done for small disturbances. Normally, only one set of solutions will be stable against the transition of the system to the state, described by the other set (or sets).

The stability of both normal and singular solutions against small perturbations can be examined by solving the Random-Phase Approximation (RPA) equation, derived in [4]. The corresponding equations determine whether an excitation with zero energy exists in the considered system, which means a possibility of a transition into another state with the same energy. For the choice of interparticle interaction (4) RPA equations are simplified and reduced to

$$1 + \alpha\chi = 0, \quad (20)$$

where χ is given by

$$\chi = \sum_j |(j|r^{-1}|i)|^2 (\epsilon_j - \epsilon_i)^{-1}. \quad (21)$$

In (21) summation should be performed over all vacant states j , which energy is given by solution of (6). In (20) $(j|r^{-1}|i)$ denotes an integral $\int \phi_j^*(\vec{r}) r^{-1} \phi_i(\vec{r}) d\vec{r}$.

Equation (20) determines the α value, at which considered Hartree state $\phi_i(r)$ becomes unstable. For interparticle interaction (14) and Hamiltonian (13) one has an instability equation similar to (20) with β instead of α and matrix elements of r^2 instead of r^{-1} in χ .

It is possible in principle, to have a situation where the normal solution and the singular one are both stable. Then these should describe two isomeric states whose energies are fairly close but whose charge distributions or sizes are very different. These states have identical quantum numbers, so a radiative transition between them is forbidden. If one of them is a ground state, the other will be metastable. It is desirable to search for such states. For the atomic case they may be excited in heavy ion collisions. The photoionization cross-sections of the ground and metastable states will also differ considerably, which might be a way to discover them.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract W-31-109-ENG-38.

REFERENCES

1. D.R. Hartree, Proc. Camb. Philos. Soc. 24 (1928) 89, 111.
2. M. Ya. Amusia and M. Yu. Kuchiev, Bulletin of Ac. Sci. of USSR, Phys. Ser. 45, 12 (1981) 12.
3. D. Thouless, The Quantum Mechanics of Many-body Systems, Academic Press, New York-London, 1961.
4. I.M. Band and V.I. Fomicher, Phys. Lett. 75A (1980) 178.
5. I.M. Band, J. Phys. B: At. Mol. Phys. 14 (1981) L649.

DATE

FILMED

3 / 23 / 94

END