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BRIEF HISTORY OF QUANTUM MECHANICAL METHODS IN ATOMIC THEORY AND HIDDEN SYMMETRIES

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Abstract

A brief review is given of some perspective methods of calculating atomic spectra and the problem of revealing hidden symmetries of effective self-consistent potentials is sketched.

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During a long history of Quantum Mechanics (QM) many effective methods for calculating atomic spectra were elaborated, the variational method and those by Hartree—Fock and Latter being included [1, 2, 3]. Nevertheless, the main problem of explaining the Mendeleev Periodicity Law attracts the vif interest both of chemists and physicists [4]. The crucial point in this Program appears to be that of revealing the hidden symmetries of the effective Hamiltonian and constructing the appropriate self-consistent atomic potential. The Demkov—Ostrovsky potential [5] gives an exclusive example of such an approximate symmetry supporting the partial explanation of the famous $(n+l)$–rule by Klechkowsky [6] and generalizing the $O(4)$–symmetry of the Hydrogen atom found by Fock [7]. The second important example is the Wiener—Della Riccia intertwinning transform [8] that sends the Hamiltonian operator from the coordinate space to the phase one, the latter property giving new opportunities for revealing additional symmetries. The main goal of our paper is to attract the attention to this original approach.

1 Brief History of QM Methods in Atomic Theory

The most popular methods of calculating atomic spectra are based on the variational approach to the stationary Schrödinger problem:

$$\langle \delta\Psi | H - E | \Psi \rangle = 0, \tag{1}$$

where H is the Hamiltonian operator of the atom, $|\Psi\rangle$ is the wave function of N electrons which is usually represented in the form of Gaunt—Slater determinant [2, 9] constructed from so-called spin-orbitals, i. e. one-electron wave functions $\phi_\alpha(q_i)$:

$$|\Psi\rangle = \det\left[\phi_\alpha(q_i)\right]. \tag{2}$$

Here q_i stands for the combined spin and coordinate variable of the i–th electron. One can deduce from (1) and (2) that the spin-orbitals prove to be eigen-functions of an effective one-electron Hamiltonian. This is the main point of the so-called self-consistent Hartree—Fock approximation [3, 10] that appears to be effective for small N only. For many-electrons atoms the modified Hartree—Fock method, the so-called Latter's one [11], is used. Within the scope of this very popular approach first one finds, following the Thomas—Fermi—Dirac

method, the average atomic potential for which the one-electron spin-orbitals are obtained and the latter ones are used for constructing the Slater determinants.

Further improvements of the Hartree—Fock method can be achieved if one takes into account the contribution of nonseparable one-electron configurations via the substitutions of the form

$$|\Psi\rangle = |\Psi\rangle_0 \left[1 + \sum \chi_{i_1 \cdots i_m} (\mathbf{r}_1, \ldots, \mathbf{r}_m)\right]. \tag{3}$$

The importance of the many-electrons configurations (3) was proved in subsequent investigations [12–15] giving rise to the so-called "cluster" method [16]. Recent years very effective methods of Quantum Field Theory were applied to atomic spectroscopy resulting in enormous simplifications of calculations [17]. However, an unexpected difficulty arose within the framework of the many-configurations approach: the sequence of the elements in the Periodic System was determined by the appropriate one-electron configuration and the energy levels were calculated via the linear combination of these configurations. The problem was in searching for the single configuration giving the main contribution to the energy of the state.

The other difficulty was caused by the relativistic effects which proved to be important for $N = Z > 55$. To take into account the relativistic behavior of the internal electrons it was suggested to use the many-electrons Dirac equation with the self-consistent potential [18].

2 Hidden Symmetry

Fock was the first who put the problem of extracting the information of the hidden or internal symmetry of atomic potentials [7]. The solution of this problem appears to be inevitable for the explanation of accident degeneracy of spectral lines. So far only the empirical rules were known to describe approximately the sequence of filling the electronic shells in atoms. The most popular rule was formulated by V.M. Klechkowsky in 1951. According to this rule, if one increases the atomic number Z, the subshells with the minimal value of $n+l$ are filled first, and if the values of this sum of quantum numbers coincide for several subshells, the preference will be given to that with the minimal n. The first reasonable explanation of this

rule was suggested by Demkov and Ostrovsky [5] who considered the radial potential of the form

$$V(r) = -\frac{ZR^2}{r(r+R)^2}, \tag{4}$$

for which the $(n+l)$-degeneracy of levels was proved for $Z > Z_k \sim k^3$, where $k = n + l$. The other fine property of the potential (4) is the experimental fact that it really approximates the self-consistent atomic potential for the elements in the middle of the Mendeleev Table.

One could imagine three possibilities to reveal such hidden symmetries extending the evident symmetry group $G = SO(3)$ of radial potentials $V(r)$. The first one concerns the standard group extension

$$G \to G' \supset G, \tag{5}$$

with the subsidiary condition being imposed, namely that the Hamiltonian H of the atom would commute with the generators L_i of the group G':

$$[H, L_i] = 0. \tag{6}$$

The second possibility concerns searching for the so-called dynamical groups [19] $G'' \supset G$, with the condition (6) being broken, that is

$$[H, M_i] \neq 0, \tag{7}$$

where M_i stand for the generators of the group G''. It is worth-while to emphasize that the generators M_i may play, due to (7), the role of ladder operators, thus allowing to estimate the spectrum of H.

At last, the third possibility concerns searching for the special intertwinning transform S having the property

$$SH = H'S, \tag{8}$$

implying that the spectra of the Hamiltonians H and H' are identical. The transform of this kind was earlier constructed in the paper [8], where the authors started with the classical Hamiltonian for N identical particles:

$$H'(p,q) = \sum_{n=1}^{N} \frac{p_n^2}{2m} + U(q). \tag{9}$$

Let us consider the scalar complex field $\varphi(p,q,t)$ defined in the phase space of the system, with the evolution equations reading:

$$\partial_t^2\varphi + L^2\varphi = 0, \tag{10}$$

where L stands for the Hermitian Liouville operator:

$$L = \imath[H',\cdot]; \quad L^2 = -[H',[H',\cdot]].$$

The energy E of the field φ can be defined as the following integral of motion:

$$E = \frac{\hbar^2}{4kT}\int dpdq\left(\dot\varphi^*\dot\varphi + [H',\varphi]^*[H',\varphi]\right). \tag{11}$$

For the stationary states of the form

$$\varphi = \exp(-\imath\omega t)\phi(p,q) \tag{12}$$

one derives from (11) and (12) that

$$E = -\frac{\hbar^2}{2kT}\int dpdq\,\phi^*[H',[H',\phi]]. \tag{13}$$

From now on we restrict ourselves to the case of factorized configurations

$$\phi(p,q) = \exp\left(-\beta\sum_n \frac{p_n^2}{2m}\right)W(q), \tag{14}$$

where β stands for some constant and $W \in L_2(\mathbb{R}^{3n})$. Substituting (14) into (13) one finds

$$E = -\frac{\hbar^2}{2kT\beta}\int dqW^*\left\{\frac{1}{2m}\triangle + \frac{\beta}{2m}\left[\triangle U - \beta\sum_n\left(\frac{\partial U}{\partial q_n}\right)^2\right]\right\}W. \tag{15}$$

As can be easily seen from (15), if one chooses $\beta = 1/2kT$ and denotes

$$\frac{1}{\hbar^2}\left[V(q)+a\right] \equiv -\frac{\beta}{2m}\left[\triangle U - \beta\sum_n\left(\frac{\partial U}{\partial q_n}\right)^2\right], \tag{16}$$

one gets from (15) the well-known expression for the energy of the quantum system with the Hamiltonian operator

$$H = -\frac{\hbar^2}{2m} \triangle + V(q). \tag{17}$$

In particular, if one considers the ground state of our quantum system $W_0(q)$ by putting

$$H\, W_0 = e_0\, W_0; \quad a = -e_0,$$

one deduces from (16) the well-known Boltzmann partition function:

$$W_0(q) = \exp\left(-\beta U(q)\right). \tag{18}$$

Let us consider some examples. The first one concerns the oscillator with the Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial q^2} + \frac{1}{2} m\omega^2 q^2. \tag{19}$$

The ground state of the oscillator being characterized by

$$W_0(q) = \exp\left(-\frac{m\omega}{2\hbar} q^2\right); \quad e_0 = \frac{1}{2}\hbar\omega, \tag{20}$$

one gets from (18) and (20) the corresponding classical potential

$$U = -kT \ln W_0^2 = \frac{mkT\omega}{\hbar} q^2. \tag{21}$$

Thus, the transformed system corresponds to the oscillator with the Hamiltonian

$$H' = \frac{p^2}{2m} + \frac{1}{2} m\nu^2 q^2 \tag{22}$$

and the new frequency

$$\nu = \sqrt{\frac{2kT\omega}{\hbar}}. \tag{23}$$

The second example concerns the Hydrogen atom with the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \triangle - \frac{e^2}{r}. \tag{24}$$

Using the ground state wave function

$$W_0 = \exp(-r/a_0); \quad a_0 = \frac{\hbar^2}{me^2}; \quad e_0 = -\frac{e^2}{2a_0}, \tag{25}$$

one deduces from (18) and (25) the classical potential

$$U = -kT \ln W_0^2 = \frac{2kT}{a_0} r \tag{26}$$

that corresponds to the J.J. Thomson's atom. The radial equations of motion in this field can be trivially integrated, the momentum being linear function of time.

3 Conclusion

We discussed three possibilities of revealing hidden symmetries in quantum atomic problems. The two of possibilities mentioned correspond to the traditional extension of the symmetry group, the Hamiltonian being involved in the set of generators. However, the third approach due to Wiener and Della Riccia reduces the quantum problem to solving the special wave equation in the phase space. The remarkable fact under this approach is the 11-correspondence between the initial and final Hamiltonians, with the spectrum being invariant.

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Comment

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Comment on BRIEF HISTORY OF QUANTUM MECHANICAL METHODS IN ATOMIC THEORY AND HIDDEN SYMMETRIES

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The aforementioned paper contains two parts. In the first one the author briefly discusses some popular methods for calculating atomic spectra, such as the variational method and those by Hartree—Fock and Latter. However, the most interesting problem is considered in the second part of the paper and concerns the origin of the so-called hidden symmetries of the effective Hamiltonian. Fock [1] was the first who attracted the attention of physicists to the problem of revealing hidden symmetries of atomic Hamiltonians. The second step was made by Demkov and Ostrovsky [2] who suggested the reasonable explanation of the famous $(n + l)$–rule by Klechkowsky giving the order of filling the electronic shells in atoms.

In the paper by Yu.P. Rybakov three possibilities of revealing the hidden symmetries are mentioned. The first one concerns the standard group extension method, where the Hamiltonian commutes

with the generators of the larger group. In the second approach one searches for the so-called dynamical group, for which the Hamiltonian serves as one of the generators. At last, the third possibility appears as the most appealing one: it concerns searching for the intertwinning transform between the old and the new Hamiltonians. As an example the author considers the Wiener—Della Riccia intertwinning transform [3] that sends the Hamiltonian operator from the coordinate space to the phase one, the latter property giving new opportunities for revealing additional symmetries.

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