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Theory of Excited States of Finite Systems in Coulomb External Potential

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Abstract.

Recently a theory of excited states of Coulomb systems (P. W. Ayers, M. Levy and Á. Nagy, Phys. Rev. A **85**, 042518 (2012)) has been put forward. The talk will present and develop this new theory. It will be shown that the Coulomb density determines the Hamiltonian and the degree of excitation. The definition of a single, universal functional which is enough to describe Coulomb systems is presented. The availability of the theory is discussed.

1. Introduction

Nowadays excitation energies are frequently calculated with time-dependent density functional theory (See, e. g. [1, 2, 3]), though there are time-independent theories, too. The first rigorous theory was the subspace theory of Theophilou [4] which was enlarged to an ensemble theory by Gross et al [5]. These approaches have, however, the disadvantage that their application to highly excited states is rather complicated and they cannot be used in case of core excitations. There also exist theories for a single excited state. The Levy-Nagy theory [6], for example, is a bifunctional theory, that is, the excited-state energy is a functional not only of the excited-state density, but also of the external potential (or the ground-state density). The Nagy theory of a single excited state [7, 8], on the other hand, is based on Kato's theorem and valid for Coulomb external potential. Recently, the latter has been generalized [9]. The talk will present and develop this new theory.

2. Cusp condition for excited states

The ground-state electron density is sufficient in principle to determine all molecular properties. This can be simply understood following Bright Wilson's [10] argument: A well-known theorem of quantum mechanics, Kato's theorem [11] leads to [12]

$$Z_{\beta} = -\frac{1}{2n(r)} \left. \frac{\partial \bar{n}(r)}{\partial r} \right|_{r=R_{\beta}}, \quad (1)$$

where the partial derivatives are taken at the nuclei β and $\bar{n}(r)$ is the angular average of the density. So the cusps of the density tell us where the nuclei are (R_{β}) and what the atomic numbers Z_{β} are. On the other hand, the integral of the density gives us the number of electrons:

$$N = \int n(\mathbf{r}) d\mathbf{r}. \quad (2)$$

Kato's theorem is valid not only for the ground state but also for the excited states. So, if the density n_k of the k -th electron states is known the Hamiltonian \hat{H} is also in principle known and its eigenvalue problem

$$\hat{H}\Psi_i = (\hat{T} + \hat{V} + \hat{V}_{ee})\Psi_i = E_i\Psi_i \quad (3)$$

can be solved, where

$$\hat{T} = \sum_{j=1}^N \left(-\frac{1}{2}\nabla_j^2\right), \quad \hat{V}_{ee} = \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad \hat{V} = \sum_{i=1}^N \sum_{\beta=1}^M -Z_J/|\mathbf{r}_i - \mathbf{R}_\beta|, \quad (4)$$

are the kinetic energy, the electron-electron and the electron-nucleon operators, respectively.

There are certain special cases, however, where Eq. (1) does not determine the atomic number. The simplest example is the $2p$ orbital of the hydrogen atom. In this case the spherical average of the derivative of the density is zero and the value of the density

$$n_{2p}(r) = cr^2 e^{-Zr} \quad (5)$$

is also zero at the nucleus. It means that in this case Kato's theorem does not give the atomic number. Similar cases occur in those highly excited atoms, ions or molecules, in which there are no s-electrons. There exist, however, a more general cusp expression for the density, that can be applied even in these special cases. The corresponding relations for the wave functions were derived by Pack and Brown [13]. (Further works concerning the cusp of the density are Ref. [14, 15, 16].) The cusp relations for highly excited states for the density were also derived [17, 18]:

$$\left. \frac{\partial \bar{\eta}_l(r)}{\partial r} \right|_{r=R_\beta} = -\frac{2Z}{l+1} \eta_l(\mathbf{R}_\beta), \quad (6)$$

where

$$\eta_l(\mathbf{r}) = \frac{n(\mathbf{r})}{r^{2l}} \quad (7)$$

and l is the smallest integer for which η_l is not zero at the nucleus. In the example mentioned above Eq. (7) leads to

$$\eta_{2p}(r) = \frac{n_{2p}}{r^2} = ce^{-Zr} \quad (8)$$

and the new cusp relation has the form:

$$-2Z\eta_{2p}(0) = 2\eta'_{2p}(0). \quad (9)$$

So we can again readily obtain the atomic number from the electron density. (Further useful cusp relations can be found in [19].) The argument above proves

Theorem 1: The density of a Coulomb system determines the external potential .

3. Theory of excited states in Coulomb external potential

Theorem 2: The excited state density n_k determines not only the Hamiltonian but the eigenvalue E_k , too.

To prove this theorem, suppose that we have two wave function Ψ_k and Ψ'_k for which the density

is the same: $n_k = n'_k$. It is well known, that the asymptotic behaviour of the density is governed by the ionization energy I [20, 21]. Consequently,

$$I_k = E_k - E_1^{(N-1)}, \quad (10)$$

where $E_1^{(N-1)}$ is the ground-state energy of the system after an electron is removed. Similarly, we can write that $I'_k = E'_k - E_1^{(N-1)}$. As the density is the same $n_k = n'_k$, so is the ionization energy $I_k = I'_k$. Therefore $E_k = E'_k$. So, for a non-degenerate state the density uniquely determines both the energy and the wave function.

Eq. (10) is valid only if

$$\varepsilon = E_1^{(N-1)} - E_k > 0, \quad (11)$$

For highly excited states ε might be negative. A more general expression valid for any excited state can be found in [21]: With the nomenclature of Wigner [22] the eigenfunctions of the Hamiltonian \hat{H}^{Coul} can be classified by the irreducible representations $D^{(l)}$, $l = 0, 1, \dots, [N/2]$. If the eigenfunction belongs to the irreducible representation $D^{(l)}$ of the symmetric group S_N , it can be ionized into $N-1$ -electron states which transform according to the irreducible representations $D^{(l)}$ or $D^{(l-1)}$ of the symmetric group S_{N-1} . Denoting by $E_{1,l}^{(N-1)}$ the lowest eigenvalue of the Hamiltonian H^{N-1} and defining

$$\tilde{E}_1^{(N-1)} = \min \left(E_{1,l}^{(N-1)}, E_{1,l-1}^{(N-1)} \right), \quad (12)$$

the decay of the wave function is determined by

$$\varepsilon_{gen} = \tilde{E}_1^{(N-1)} - E_k. \quad (13)$$

The present theory is valid provided this quantity is positive, that is, for a bound state.

Define now the functional F .

$$F[n] = E - \int n(\mathbf{r})v(\mathbf{r})d\mathbf{r} \quad (14)$$

is valid for any stationary state of any Coulomb system. As there is no known way to decide (without constructing the external potential and solving the Schrödinger equation), whether a given density is Coulombic it would be better to define a functional F for all electron densities.

First, F is defined as a functional of a trial density n and a Coulomb density n^{Coul} corresponding to the the k th state of some Coulomb Hamiltonian

$$F[n, n^{Coul}] = \min_{\substack{\Psi \rightarrow n \\ \{\langle \Psi | \Psi_j^{Coul}[n^{Coul}] \rangle = 0\}_{j=1}^{k-1}}} \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle. \quad (15)$$

The minimization is done with the constraints that each Ψ yield $n(\mathbf{r})$ and is simultaneously ortogonal to the first $k-1$ states of the Coulomb system specified by $n^{Coul}(\mathbf{r})$. Then a universal functional $F[n]$ can be constructed as follows. Assume that there exists a unique Coulomb density that is closest to the (non-Coulomb) density n . (The best measure for "closest" is not detailed here.) If there are several Coulomb densities from the same 'distance' from n , the one yielding to the smallest F (Eq. (15)) is selected:

$$F_\epsilon^{Coul}[n] = \min_{n^{Coul}} F[n, n^{Coul}]; \quad ||n^{Coul} - n|| \leq \epsilon. \quad (16)$$

ϵ is supposed to be large enough to ensure the existence of at least one stationary state Coulomb density in the distance smaller than ϵ . With ϵ_{min} denoting the smallest possible value of ϵ ,

$$F^{Coul}[n] = F_{\epsilon_{min}}^{Coul}[n]. \quad (17)$$

This procedure should be done in the “vicinity” of all Coulomb densities $n_k(\mathbf{r})$. In this way the functional F^{Coul} is defined for any density. Supposing that this functional is functionally differentiable we are led to the Euler equation

$$v^{Coul}([n], \mathbf{r}) = -\frac{\delta F^{Coul}[n]}{\delta n} \quad (18)$$

up to a constant. The theory presented here is for non-degenerate states. The generalization for degenerate states will be published elsewhere. An extension to the Kohn-Sham scheme is under progress.

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