A MODEL HAMILTONIAN FOR THE PERIODIC TABLE

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(Recibido: noviembre 3, 1971)

ABSTRACT: In order to predict the building-up of the many-electron atomic ground states, we propose a model Hamiltonian with one adjustable parameter, related to the assymmetric point rotor in Fock's projected momentum space. With the exception of the $5d$ level, the correct ordering is achieved.

The independent-particle model has been fruitfully used in the treatment of the ground states of complex atoms[1]. Such an approximation, however, has the disadvantage that it implies the familiar n^2-fold degenerate hydrogen-like spectrum, while the empirical ordering is

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$$1s < 2s < 2p < 3s < 3p < 4s \lesssim 3d < 4p < 5s \lesssim 4d < 5p < 6s \lesssim 4f \lesssim 5d < 6p < 7s \tag{1}$$

and exhibits a dependence on n and l. This has suggested the Aufbau scheme[2] which reproduces the ordering (1) by proposing to count the levels by increasing values of $n + l$ and l.

The lack of rigour in such a scheme has been often criticized[3, 4] However, the construction of an *effective* Hamiltonian whose independent-particle states can exhibit the level ordering (1) is quite important[3].

This has been attempted by starting from the real many-body Hamiltonian, modified through some physical considerations as in the well-known Hartree-Fock approximation[5] or by starting from an intrinsically broken symmetry[6].

In this note we shall proceed to build, in a formal way, a *model* Hamiltonian (which is not expected to be related to that of many-electron systems) which through the use of a single adjustable parameter can reproduce (1) quite well. Such a construction is suggested by analogy with the one-electron Coulomb system.

Indeed, we use the Fock mapping[7] to implement the isomorphism between the Coulomb system and the spherical four-dimensional point rotor to translate the Hydrogen atom Schrödinger equation

$$H\psi_{nlm}(\mathbf{r}) = -\frac{E_B}{n^2}\,\psi_{nlm}(\mathbf{r}), \quad \begin{array}{l} n = 1, 2, \ldots \\ l = 0, 1, \ldots n-1 \\ |m| \leqslant l \end{array} \tag{2a}$$

where E_B is the Bohr energy, into the equation

$$\Lambda^2\, \mathcal{Y}_{\nu lm}(\Theta) = \nu(\nu + 2)\, \mathcal{Y}_{\nu lm}(\Theta) \tag{2b}$$

which characterizes the four-dimensional spherical harmonics $\mathcal{Y}_{\nu lm}(\Theta)$ on the four-sphere space (Θ) as eigenfunctions of the SO(4) second-order Casimir operator

$$\Lambda^2 = \sum_{i>j=1}^{4} \Lambda_{ij}^2 \tag{2c}$$

relating the principal quantum numbers as $\nu = n - 1$, the meaning of l and m

being the same. The spherical rotor Hamiltonian is expressible as $\Lambda^2/2I$, where I is the moment of inertia.

The assymmetric rotor, however, has a Hamiltonian

$$H_R = \sum_{i>j=1}^{4} \frac{\Lambda_{ij}^2}{2I_{ij}} \tag{3a}$$

where I_{ij} is the moment of inertia in the i-j plane. In particular, an assymmetric rotor with an SO(3) symmetry around the 4-axis can be described through the Hamiltonian

$$H_R = \frac{1}{2I}(\Lambda^2 + \alpha L^2) \tag{3b}$$

(where L^2 is the SO(3) second-order Casimir operator) with the same eigenfunctions as (2b), with eigenvalues proportional to $\nu(\nu+2) + \alpha l(l+1)$. This simple scheme, mapped back to the Coulomb system provides a model Hamiltonian whose energy levels

$$E_{nl} = -E_B\,[n^2 + \alpha l(l+1)] \tag{3c}$$

are raised for higher angular momenta l and which, for the values $1.65 < \alpha < 1.75$ yields a spectrum whose levels are ordered as (1) except for the 5*d* level which comes out slightly lower than both 6*s* and 4*f*. It is well known[5] that the level ordering (1) is only approximately true as the *nd* levels sometimes shift *down* producing the rare-earth behaviour. Such level shifting however, is associated with spin properties and consequently this simple scheme cannot be expected to give a detailed description of it.

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RESUMEN

Se propone un hamiltoniano modelo para predecir el ordenamiento de los estados base de átomos con muchos electrones. El hamiltoniano modelo, que depende de un parámetro ajustable, está relacionado al rotor puntual en el espacio momental proyectado de Fock. Con excepción del nivel $5d$, se obtiene el orden correcto.