Effective Operators and Rydberg States

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Amaldi and I experimented on sodium. During these experiments we observed high quantum states, corresponding to enormous orbits. I called them "swollen atoms"; today more scientifically, but less pictorially, they are called "Rydberg states".

—Emilio Segré, *A Mind Always in Motion,*Univ. California Press, Berkeley, 1993 p83

Some recent references

(1). B Zygelman, *Non-Abelian Geometric Phase and Long -Range Atomic Forces*, Phys. Rev. Lett. **64**, 256 (1990)

(2). W Clark, C H Greene and G Miecznik, *Anisotropic Interaction Potential between a Rydberg Electron and an Open Shell Ion*, Phys. Rev. **A53**, 2248 (1996)

(3). W Clark and C H Greene, *Anisotropic interactions in autoionizing Rydberg systems*,
Phys. Rev. **A56**, 403 (1997)

(4). W Clark and C H Greene, *Adventures of a Rydberg electron in an anisotropic world*, Rev. Mod. Phys. **71**, 821 (1999)

Anisotropic interactions and Rydberg States

1. Consider the case of a non-penetrating Rydberg electron ℓ that roams beyond an open-shell core with angular momentum L_c.
2. Zygelman predicted that such systems should exhibit a "vector" interaction in the long range potential of the form

$$\beta_v \frac{(\mathbf{L}_c \cdot \ell)}{r^6}$$

3. Greene and his colleagues have shown that the inclusion of such a term does indeed lead to an improved parametric fit to the observed spectra and discussed in some detail its origin and noted that a similar such term was introduced in atomic spectroscopy "*on semiemprical grounds and without an explicit derivation or formal justification*".

> *"When a thing was new, people said,'It is not true'. Later when its truth became obvious, people said, 'Anyhow, it is not important' and when its importance could no longer be denied, people said, 'Anyway, it is not new."* —William James

Effective interactions in open shell atoms and ions

1. Consider a two-electron configuration ℓ^2. There are $(2\ell+1)$ terms SL. The scalar Coulomb interaction involves $(\ell+1)$ Slater radial integrals. Suppose these are treated as parameters to be fitted to experimentally observed SL terms. We do not expect to get a very good fit as we are ignoring configuration interaction effects.
2. In the 1950's Trees[5–7] and Racah[8] found emprically that adding a term $\alpha L(L+1)$ led to a significant reduction in the mean least squares error between the experimental and calculated energies of the SL terms for d^n shell ions. No explanation for the introduction of this effective interaction was offered.
3. In 1959 Runciman and Wybourne[9] found that the introduction of a term $\alpha L(L+1)$ significantly improved the calculation of the terms of the $4f^2$ and $4f^{12}$ configurations for the trivalent

(5). R E Trees, *Configuration Interaction in MnII*, Phys. Rev. **83**, 756 (1951)

(6). R E Trees, *Term Values in the* $3d^5 4s$ *Configuration of FeIII*, Phys. Rev. **84**, 1089 (1951)

(7). R E Trees, *The* $L(L+1)$ *Correction to the Slater Formulas for the Energy Levels*, Phys. Rev. **85**, 382 (1952)

(8). G Racah, $L(L+1)$ *Correction in the Spectra of the Iron group*, Phys. Rev. **85**, 381 (1952)

(9). W A Runciman and B G Wybourne, *Spectra of Trivalent Praseodymium and Thulium Ions*, J. Chem. Phys.,**31**, 1149 (1959)

4. Back in 1934 Bacher and Goudsmit[10] had demonstrated that most, though not all, of the second-order electrostatic interactions can be added linearly. They used linear relations to express the unknown energy levels in terms of *observed* energy levels of the atom and its ions.
5. Trees and Racah sought to replace the second-order effects by the first-order terms of an *effective* two-body interaction.

(10). R F Bacher and S Goudsmit, Phys. Rev. **46**, 948 (1934)

The "Linear" Theory of Configuration Interaction

1. The central idea of the "linear" theory was to augment the Hamiltonian for an $N-$electron system with additional two-body *scalar* interactions.
2. Associated with each interaction is an adjustable parameter.
3. The number of adjustable parameters is chosen to equal the number of allowed SL terms occurring in all distinct two-electron congifurations that may be formed by deleting $N-2$ of the electrons from the configuration under study.
4. We take into account the distortion of a pair of electrons by interactions with other configurations and then generalise the result to say that the distortions add linearly when we form an $N-$electron system.

Example of f^N Configurations

Here $\ell = 3$ and we need 7 adjustable parameters. Four come from the Coulomb interaction, E_0, E_1, E_2, and E_3 in Racah's notation, or equivalently the Slater integrals, F_0, F_2, F_4 and F_6. The remaining three may be chosen as

$$\alpha L(L+1) + \beta C(G_2) + \gamma C(SO_7) \qquad (1)$$

where the last two are the Casimir invariants of the groups G_2 and SO_7.

Origin of the Corrections

1. In 1962 I attempted, with K Rajnak[11] to make an explicit derivation of the effective interactions portrayed in Eq. (1) by using second-order perturbation theory and summing over the states of generic configurations that could couple to a configuration ℓ^n of n equivalent ℓ electrons. In the particular case of $\ell = 3$ we did indeed obtain Eq.(1) complete with expressions for the relevant parameters.
2. It was found that most of the second-order effects were accommodated by Eq.(1) together with terms simply proportional to the Slater radial integrals.
3. In addition non-linear terms involving effective three-body terms were discovered.
4. Thus the Trees and Racah observations have been given an interpretation.

(11). K Rajnak and B G Wybourne, *Configuration Interaction Effects in l^n Configurations,* Phys. Rev.,**132**, 280 (1963)

He who can, does; he who cannot teaches
George Bernard Shaw, *Man & Superman (1903)*

The Orbit-Orbit Interaction

1. It is worth noting that the orbit-orbit interaction in an electron configuration ℓ^n can be expressed in terms of ℓ scalar two-body operators of odd rank just like for configuration interaction BUT with the opposite sign coefficients.
2. The above remark highlights the danger of assuming that a parametric fit to data vindicates our assumed interactions. Without an *abinitio* calculation we cannot be sure that a specifically omitted interaction is the reason for the fit.

(12). B G Wybourne, *Orbit-orbit Interactions and the 'Linear Theory' of Configuration Interaction*, J. Chem. Phys. **40**, 1457 (1964)

> *"It did, Mr widdershins, until quantum mechanics came along. Now everything's atoms. Reality is a fuzzy business, Mr Widdershins. I see with my eyes, which are a collection of whirling atoms, through the light, which is a collection of whirling atoms. What do I see? I see you Mr Widdershins, who are also a collection of whirling atoms. And in all this intermingling of atoms who is to know where anything starts and anything stops. It's an atomic soup we're in, Mr Widdershins. And all these quantum limbo states only collapse into one concrete reality when there is a human observer"*
>
> —Pauline Melville, *The Girl with the Celestial Limb (1991)*

One Electron outside of a Shell of Equivalent Electrons[13]

1. Consider a $N+1-$electron configuration $n\ell^N n'\ell'$. Let $\ell_<$ be the lesser of ℓ and ℓ'.
2. There are $(2\ell_< + 2)$ radial integrals associated with the Coulomb interactions between the $n\ell^N$core ($c = core$) and the $n'\ell'$ electron.
3. The total second-order linear distortion involves $2\ell_<$ additional parameters.
4. In the case of $\ell_< = 1$ we can take the two additional terms as
$$\alpha L(L+1) + \beta S(S+1)$$
5. More generally, we can consider operators of the type
$$(\mathbf{U}_c^{(2i+1)} \cdot \mathbf{u}^{(2i+1)}) \quad (1)$$
$$(\mathbf{V}_c^{(1,2i)} \cdot \mathbf{v}^{(1,2i)}) \quad (2)$$
where in each case $i = 0, 1, \ldots, \ell_<$. For $i = 0$ in (1) the term is, to within a proportionality constant, just
$$(\mathbf{L}_c \cdot \mathbf{l})$$
which is of the same structural form as the so-called "vector interaction" introduced by Zygelman.
6. Note that the other operators appearing in (1) will mix core states.

(13). B G Wybourne, *Generalization of the "Linear Theory" of Configuration Interaction*, Phys. Rev. **137**, A364 (1965)

Concluding Remarks

Parametric treatments of spectral levels occur in many different contexts. One needs to remember that they are simply parametric treatments and as such can hide much of the real physics. In many cases agreement with experiment simply means that the symmetry properties of the system have been correctly identified. In mathematics one is constructing the elements of an integrity basis, the minimal set of invariants in which all other invariants are polynomials in that minimal set. The physics comes in the *abinitio* evaluation of the different contributions leading, ultimately, to a description of the empirically deduced parameters.

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Questions?

"The only questions worth asking are the unanswerable ones"

—John Ciardi, *Saturday Review-World (1973)*

"To Every Complex Question there is a Simple Answer – And it's Wrong."

—H L Mencken

"Those who can, do; those who can't attend conferences"
Daily Telegraph 6th August (1979)

Thankyou!