MULTI-DIMENSIONAL ELECTRONIC AND NUCLEAR COORDINATES INFLUENCING LASING ACTION

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Abstract-The easy, and some far more counterintuitive, parts of quantum mechanics are analyzed for monatomic ions; for the time-independent Schrödinger solution for a given set of N nuclei and a number of electrons; and if the Born-Oppenheimer factorization is acceptable, the $(3N-5)$ dimensional potential surfaces of each electronic state are significant for Stokes shifts of asymmetric luminescence bands, and unexpected shape and positions of new absorption bands due to laser-induced quasi-stationary small concentrations of a low-symmetry excited state.

Rather than using popular approximations to quantum chemistry for spectra of systems with several (N) nuclei without critical analysis, it may be worthwhile for laser experts to contemplate useful, as well as heavily impeding, consequences of the Schrödinger equations from 1926. The difficulties can be arranged [1] in stratifications: the monatomic entities with one Z nucleus surrounded by K (at most $Z+1$) electrons [the observed energy levels of lanthanides [2,3] are similar to J -levels of $4f^q$ with $q = (Z-57)$ for Ln(III) and $(Z-56)$ for Ln(II)]; the time-independent Ψ of a set of N nuclei $Z_1, Z_2, \dots, Z_N$ surrounded by a given number of indiscernable electrons; and the time-dependent behaviour, including radiative transitions from Z_1 to Z_2 , and also non-radiative de-activations (including photochemistry).

A fourth stratification is that the Born-Oppenheimer factorization is an excellent approximation (although intensity of overtone [4] vibrations and certain couplings between an excited state and the surroundings can be higher-order deviations). For $N=1$, Ψ is a product

of a translational factor with 3 spatial variables, times the electronic state Ψ_{elec} involving 3K variables. For more than one nucleus, two additional factors are the rotational Ψ_{rot} (with 3 degrees of freedom, except 2 for N=2) and the vibrational factor Ψ_{vib} (with one internuclear distance R for N=2, and (3N-6) mutually independent distances for N at least 3). Each electronic state then has a vibronic potential surface (having various Ψ_{vib} as Schrödinger solutions). Since its energy E_{ps} depends on the set of (3N-6) R_{12} values, this potential surface subsists in a (3N-5) dimensional space for N above 2 (16 dimensions for MX_6 or any other case of 7 nuclei).

Some chemists feel alienated [3-6] by these facts [and indeed, quantum chemistry may be almost hopeless as deductive (rather than as inductive parametrization) rationalization, when two-digit Z values occur]. The difficulty goes all the way back [1] to N=1 such as gaseous Gd^{+3} with K=61 having 183 Cartesian variables in Ψ_{elec} . A small hope remains that 6 dimensions might be sufficient in a second-order density matrix (but a criterion replacing the variation principle has not yet been found). Six dimensions are a minimum requirement, both in a helium atom and in gadolinium(III) compounds having their first excited level $^6P_{7/2}$ at 3.9 eV (higher [1,5] than the typical heat, per atom, of atomization of compounds). This $4f^7$ system has attracted attention [7-9] as an example of the problems for Slater-Condon-Shortley [S.C.S.] treatment of (S,L) term distances of a partly filled 1^q shell as due to differing interelectronic repulsion. Katriel and Pauncz [10-12] analyzed the counterintuitive consequences of the virial theorem (already for K=6). Much more devastating is the intermixing of electron configurations, providing [3,11] a correlation energy $-E_{\text{corr}}$ of order $(0.7 \text{ eV})Z^{1.2}$ roughly proportional to the square root of the Gáspár approximation $E_G = (13.6 \text{ eV})Z^{2.40}$ to the total binding energy [11] of the Z electrons in a neutral atom. Not only is the first ionization energy I_1 smaller than $-E_{\text{corr}}$ for all atoms with Z above 10, but the squared amplitude of the Hartree-Fock Ψ in the groundstate Schrödinger (non-relativistic) Ψ_{elec} decreases from 0.99 in helium to 0.93 in neon (Z=10), and an (admittedly crude) argument [3] of second-order perturbation suggests this "squamp" to be 0.7 for zinc (Z=30) and 0.4 for neodymium (Z=60). If the "squamp" is of order a-half in xenon atoms and in lanthanides, only half of the total resulting properties is determined by the conventional electron configuration (called the "preponderant" configuration [13,14] for the purpose of defining

oxidation states). This Pandora box is aggravated by chemical bonding; although $-E_{\text{corr}}$ may be only 50 or 200 percent larger than for the sum of the constituent atoms, its increase (mainly due to valence shells and some empty orbitals) may correspond to a dramatic decrease of the "squamp" in condensed matter.

An excited electronic state (living longer than 10^{-7} s) is called a "thexi" [thermally equilibrated (as far as vibrations go) excited] state by Adamson[15]. It can already occur in lanthanides, such as $^6P_{7/2}$ of Gd(III) aqua ions luminescing several milliseconds, showing distinct chemistry[3,4] and moderate co-excitation of vibrations in emission. Typical $3d^q$ excited states, such[16] as 2E of Cr(III) may be similar, suggesting potential surfaces parallel to the 4A_2 groundstate. The broad band absorption and (near infrared) luminescence of 4T_2 corresponds to one anti-bonding d-like electron with concomitant[16] longer Cr-X distances, and large Stokes shift. It is an oversimplification[6,17] to consider only totally symmetric "breathing" (at a given moment having all R_{12} multiplied by the same factor close to 1). The excited states showing two orbitals with identical energy in high symmetry (O_h) unequally populated by (1 and 0; or 2 and 1) electrons distort their symmetry (like d^q Jahn-Teller effect) and emit asymmetric luminescence bands, and, what is very important for lasers[6,17] develop intense transitions (frequently camel- rather than dromedary-shaped) to even higher states, impeding population inversion (because of parasitic absorption). The first excited 4T_1 of manganese(II) [having one anti-bonding electron less than the groundstate 6A_1] shows numerous excited quartets, preventing lasing[18]. The intricate discrepancies between the pragmatic S.C.S. parameters and Hartree-Fock integrals of interelectronic repulsion have been discussed[1,19-21]. A source of unexpected quenching can be crossing or near-crossing of the (3N-5) dimensional "thexi" potential surfaces with electron transfer states[3,13,22,23] having their manifold of R_{12} at quite unfamiliar, low symmetry.

Newtonian mechanics is excellent for describing motion of planets, their moons, and space probes (slightly less for comets losing mass) in the Solar system. We all know it is less compelling, when friction occurs, and probably not able to give now the weather forecast 28 April next year. We should not be worried, when quantum mechanics rapidly gets less convincing when the number of electrons and/or nuclei increases, or the time-dependent processes become predominant. Spectroscopists and chemists should not take sleeping pills for their critical sense.

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