PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Glossary

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Glossary

A brief guide to the argot of Rydberg spectroscopy

1. Concepts

autoionization decay of a semi-discrete level above the ionization limit into the ionization continuum

Beutler–Fano profile line shape for a transition to a semi-discrete state interacting with an overlapping continuum

bright states states to which transitions are allowed in a particular experiment

channel in scattering formulations of Rydberg states, there is a channel for each state of the core; each Rydberg state has multiple quantum defects, one corresponding to each channel

core the positive ion, relative to which a Rydberg electron occupies a (usually) large orbital

dark states states to which transitions are forbidden in a particular experiment, often those with high l

Edlén plot a plot of quantum defects of a Rydberg series, for an assumed IP, versus energy; the correct IP should give a limiting straight line at high ν

$f_{\nu l}(r)$, $g_{\nu l}(r)$ regular and irregular radial wavefunctions for a Coulomb potential, where r is the electron–core distance; for bound levels, the combination $\cos\pi\nu f_{\nu l}(r)+\sin\pi\nu g_{\nu l}(r)$ satisfies the boundary condition at $r\rightarrow\infty$

frame transformation orthogonal transformation between approximate descriptions of a Rydberg orbital at different electron–core distances r; for example, change from Hund's case (b) to case (d) angular momentum coupling with increasing r

half-collision a scattering formulation with no incoming channel

***K*-matrix** reaction matrix, occurring in the basis function $f_i(r)-\sum_j K_{ij}(r)g_j(r)$ for channel i

$\mathcal{L}\equiv l_N$ the quantum number $(N-N^+)$, the projection of $\boldsymbol{l}$ on the direction of $\boldsymbol{N}$ or $\boldsymbol{N}^+$, which are essentially parallel for $l\ll N\approx N^+$

***l*-complex** a group of states that correlate with a single value of l in the united atom

Lu–Fano plot a plot of multiple quantum defects (modulo 1) against each other; particularly useful in the analysis of perturbed Rydberg series

μ quantum defect $n-\nu$, often taken modulo 1, also denoted δ; in multichannel treatments there is a (diagonal) quantum defect for each channel, and, more generally, there is a quantum defect matrix $\mu_{ij}=(1/\pi)\tan^{-1}K_{ij}$ with both diagonal and off-diagonal elements

$\nu\equiv n^*$ effective principal quantum number

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ν scaling for $\nu \gg l$, regular Coulomb-type radial functions behave as

$$f_{\nu l}(r) \sim \frac{1}{\nu^{3/2}(2l+1)!}\left(\frac{Z}{a_0}\right)^{1/2}\left(\frac{2Zr}{a_0}\right)^{l+1}$$

for $r \sim 0$; from the normalization factor, operators O with a short range in r (e.g. spin-orbit coupling or core–Rydberg interactions) have Rydberg–Rydberg matrix elements $\langle\nu'|O|\nu\rangle$ proportional to $(\nu'\nu)^{-3/2}$, and core–Rydberg matrix elements $\langle\mathrm{core}|O|\nu\rangle$ proportional to $(\nu)^{-3/2}$

penetration significant amplitude of a Rydberg orbital within the core

+ superscript used for quantum numbers and parameters of the core

precursor an orbital of the core with a similar angular distribution, such as the same united-atom l and λ, as the Rydberg orbital under study; the presence of an occupied precursor orbital raises the energy of the Rydberg orbital

recombination usually refers to electron capture by an ion X^+ to produce (initially) Rydberg states of the neutral species X

Rydberg (*Ry*) term unit, such that the ionization potential of an orbital (in wavenumber units) is $\mathrm{IP} = Z^2 Ry/\nu^2$, where Z is the charge number of the core and ν is the effective principal quantum number; Ry depends on the core mass M^+ according to $Ry = (1 + m_e/M^+)^{-1} Ry_\infty$, where $hcRy_\infty = \frac{1}{2}E_h$, and E_h is the atomic unit of energy (the hartree); *ab initio* calculations are usually for infinite core mass

Rydberg orbital a large (or diffuse) atomic or molecular orbital that is largely separable from the orbitals of the core

Rydberg series a series of levels or transitions of the same character (e.g. the same $l\lambda$), with near-integer separations between successive values of ν

Rydbergization the transformation of a valence molecular orbital at longer internuclear distances to a united-atom Rydberg orbital at shorter internuclear distances

$\mathcal{S} \equiv s_J$ the quantum number $(J - N)$, the projection of $\boldsymbol{s}$ on the direction of $\boldsymbol{J}$ or $\boldsymbol{N}$, which are esentially parallel for $s \ll J \approx N$

supercomplex a set of l-complexes that interact with each other, such as interacting s and d complexes

2. Abbreviations

BO Born–Oppenheimer

CI conical intersection; configuration interaction

DR dissociative recombination; double resonance

IC internal conversion

IP ionization potential

IR infrared

JT Jahn–Teller

MATI mass-analysed threshold ionization

MPI multiphoton ionization

MQDT multi-channel quantum defect theory

OODR optical-optical double resonance

PES photoelectron spectroscopy; potential energy surface

PFI pulsed field ionization

PTS photofragment translational spectroscopy

QDT quantum defect theory

REMPI resonance-enhanced multiphoton ionization; the numbers of photons are given by a notation $(M + N)$, where the resonance occurs at M photons and the ionization at N more photons; if two frequencies are used, one is denoted by a prime, etc.; thus $(2 + 1)$ one-colour REMPI or $(3 + 1')$ two-colour REMPI

SEP stimulated emission pumping, involving PUMP and DUMP lasers

TKER total kinetic energy release

TOF time of flight

UV ultraviolet

VUV vacuum ultraviolet, typically $1200 \leqslant \lambda \leqslant 2000$ Å

XUV extreme ultraviolet, typically $500 \leqslant \lambda \leqslant 1200$ Å

ZEKE zero electron kinetic energy

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