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LETTERS

Quantum-Defect Theory of Excited $^1\Pi_u^-$ Levels of H_2

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Quantum-defect methods are used to calculate, by a single unified procedure, the full spectrum of $J=1$ $^1\Pi_u^-$ Rydberg levels of H_2, extending from the lowest levels of the $2p\pi^-$ $C^1\Pi_u^-$ state to the high members of the $np\pi^-$ series between the $H_2^+(v=0)$ and $H_2^+(v=1)$ ionization thresholds. Results for the C state are substantially improved over previous calculations based on direct integration of the vibrational Schrödinger equation, while results at higher energies reproduce with high accuracy the recently observed spectrum, including local perturbations.

We have carried out, by a single unified procedure, a calculation of the full spectrum of $J=1$ Rydberg levels in H_2 of $^1\Pi_u^-$ symmetry, corresponding to an excited $np\pi^-$ electron, from the lowest levels of the $2p\pi^-$ $C^1\Pi_u^-$ state to the higher members of the $np\pi^-$ series between the $H_2^+(v=0)$ and $H_2^+(v=1)$ ionization thresholds. The calculation is the first application of the channel-interaction methods of quantum-defect theory[1] to electron-vibration interactions.[2,3]

The calculation is based on an R-dependent quantum defect $\mu_{p\pi}(R)$ (R is the internuclear distance) derived from the accurate *ab initio* (fixed-nuclei) potential-energy curve for the C state.[4] This single function $\mu_{p\pi}(R)$, together with the vibrational wave functions of the $H_2^+(v)$ $1s\sigma X^2\Sigma_g^+$ state, serves to characterize completely the vibration-electron interaction throughout the full spectrum of Rydberg levels: The deviation from

experiment of the calculated levels of the C state is reduced by as much as 2 orders of magnitude compared to values obtained by direct integration of the vibrational Schrödinger equation with the C-state potential[5]; at the same time the predicted positions of the higher members of the $np\pi^-$ series ($J=1$) correspond closely to the spectrum of $Q(1)$ lines of the $np\pi$ $^1\Pi_u^- - X^1\Sigma_g^+$ bands, based on accurate measurements which have just recently become available.[2,6]

Most previous work on vibration-electron coupling was based on the Born-Oppenheimer approximation. Effects of the breakdown of this approximation were accounted for at best by successively introducing diagonal correction terms (adiabatic approximation) and nondiagonal interaction between electronic states (nonadiabatic effects). The power of the quantum-defect method is that it builds the interaction between electron-

ic and molecular rotational and vibrational mo-
tions into the theory from the start by referring
to the two extreme situations (A and B)[1] of com-
pletely coupled nuclear and electronic motion and
completely independent nuclear and electronic
motion. Situation A prevails when the electron is
a short distance from the molecular core; the
difference $\Delta\epsilon$ between electronic levels ($\epsilon = -\Re/n^{*2}$ for discrete states, where $\Re$ is the Rydberg
constant and n^* the effective quantum number) by
far exceeds the vibrational spacings, $|\Delta\epsilon| \gg \omega$
(n^* small), and the electronic motion is fast com-
pared to that of the nuclei. Situation B pertains
to large electron–molecular-core separation; $\Delta\epsilon$
is then small compared to the vibrational spac-
ings, $|\Delta\epsilon| \ll \omega$ (n^* large), and the electronic mo-
tion can no longer effectively follow that of the nu-
clei.

Thus, in situation A the Born-Oppenheimer ap-
proximation is valid. Here one can average over
the fast electronic motion at each internuclear
distance R, and use a quantum-defect expression
of the total electronic energy, i.e., a sum of core
and Rydberg electron energies,[2,3,7]

$$U^{np\pi}(R) = U^+(R) - \Re/[n - \mu_{p\pi}(R)]^2, \qquad (1)$$

as the potential for the vibrational motion. The
fixed-nuclei potential-energy curve $U^+(R)$ of the
core consists of the energies of the core electron
plus nuclear repulsion. The contribution of the
Rydberg electron to the bonding of the molecule
determines the quantum-defect function $\mu_{p\pi}(R)$.
A key feature is that $\mu_{p\pi}(R)$ is independent of the
degree of electronic excitation.

In situation B the slow motion of the electron
relative to the nuclear motion means, on the
other hand, that the positions of the Rydberg lev-
els are now characterized by the vibrational quan-
tum number v of the core. Thus these levels are
obtained by averaging $\mu_{p\pi}(R)$ over the vibrational
motion of the core,[2] i.e.,

$$T(v)(J=1) = T^+(v)(N=1) - \Re/[n - \mu_{p\pi}(v)]^2, \qquad (2)$$

where

$$\pi\mu_{p\pi}(v) = \arctan M_{vv}, \qquad (3)$$

and

$$M_{vv'} = \int \chi_v^+(R) \tan[\pi\mu_{p\pi}(R)] \chi_{v'}^+(R)\, dR. \qquad (4)$$

The $T^+(v)(N=1)$ are the (exact) vibrational levels
of the ion with rotational quantum number $N = 1$
and the $\chi_v^+(R)$ are the corresponding vibrational
wave functions. Note that Eq. (2) describes the
situation opposite to that implied by the Born-

Oppenheimer approximation.

As n increases along the Rydberg series, the
Rydberg electron roams farther and farther from
the molecular core and a transition from situa-
tion A to situation B occurs. This transition cor-
responds to an uncoupling of the electronic mo-
tion from the vibrations of the core, and is the
vibrational analog of the rotational l uncoupling
well known to spectroscopists. Thus adiabatic
and nonadiabatic effects in electronic states of
low excitation are early stages of the uncoupling
towards situation B. At the other extreme, local
perturbations between high members of series
converging to different limits $T^+(v)(N=1)$ are
precursors of the departure toward situation A.
The quantum-defect theory unifies these alterna-
tive extremes by means of the unitary transform-
ation connecting the eigenfunctions of electronic
motion in situation A, characterized by the (fixed)
internuclear distance R, and the eigenfunctions
of electronic motion in situation B, character-
ized by the vibrational quantum number v of the
residual ion. The matrix elements of this unitary
transformation are $(R|v)$, i.e., just the vibration-
al wave functions $\chi_v^+(R)$.[3,8]

This analysis[3] expresses the level positions

$$T = T^+(v)(N=1) - \Re/[n^*(v)]^2 \qquad (5)$$

in terms of an eigenvalue problem of a type intro-
duced by Seaton,[9] i.e.,

$$\det |\tan[\pi n^*(v')]\delta_{vv'} + M_{vv'}| = 0. \qquad (6)$$

The solution of Eq. (6) has been carried out in
two steps. First, the quantum-defect function
$\mu_{p\pi}(R)$ was calculated using Eq. (1) with $n = 2$ and
the (fixed-nuclei) curves $U^+(R)$ of Wind[10] and
$U^{2p\pi}(R)$ of Kołos and Wolniewicz.[4] This function
was then used to calculate the matrix elements
$M_{vv'}$ for $0 \leq (v, v') \leq 6$. In a second step Eq. (6)
was solved using the following additional theo-
retical input data: (i) the H_2^+ vibrational levels
$T^+(v)(N=1) - T^+(0)(N=0)$ obtained by Beckel, Han-
sen, and Peek,[11] and (ii) the ionization potential
$T^+(0)(N=0) = 124\,417.3$ cm^{-1} of Hunter and Pritch-
ard (see Ref. 2).

Some of the results obtained in this way are
listed in Tables I and II. Table I concerns a case
close to situation B, namely the energy region
between the $v = 0$ and $v = 1$ ($N = 1$) ionization limits.
Theoretical and experimental levels agree within
less than 1 cm^{-1} for almost all cases. Figure 1
shows a quantum-defect plot of the same data.
For each level n the quantum defect $n - n^*$ with
respect to the $v = 1$, $N = 1$ limit is plotted against

TABLE I. Experimental and theoretical energies of $np\pi^-$, $J = 1$ levels of H_2 between the $v = 0$ and $v = 1$ ($N = 1$) ionization limits (in units of cm^{-1}).

Approximate description[a]	Observed[b,c]	Theoretical[c]
$16p\pi^-$ $v = 1$ $J = 1$	126 240.1	126 239.9
$15p\pi^-$ $v = 1$ $J = 1$	126 182.6	126 181.8
$14p\pi^-$ $v = 1$ $J = 1$	126 111.2	126 111.0
$13p\pi^-$ $v = 1$ $J = 1$	126 023.5	126 023.3
$12p\pi^-$ $v = 1$ $J = 1$	125 913.2	125 913.0
$11p\pi^-$ $v = 1$ $J = 1$	125 774.9	125 775.3
$6p\pi^-$ $v = 2$ $J = 1$	125 763.1	125 764.3
$10p\pi^-$ $v = 1$ $J = 1$	125 585.6	125 585.4
$9p\pi^-$ $v = 1$ $J = 1$	125 335.1	125 335.3
$8p\pi^-$ $v = 1$ $J = 1$	124 985.8	124 986.7
$5p\pi^-$ $v = 2$ $J = 1$	124 501.5	124 503.8
$7p\pi^-$ $v = 1$ $J = 1$	124 471.4	124 473.0

[a] Assuming situation B.
[b] From Herzberg and Jungen, Ref. 2.
[c] Above $v = 0$, $J = 0$ of $X^1\Sigma_g^+$.

TABLE II. Experimental and theoretical energies of $J = 1$ levels of the $C^1\Pi_u^-$ state in H_2 (in units of cm^{-1}).

Approximate description[a]	Observed[b,c]	Theoretical[c] This work	Theoretical[c] Ref. 5[d]
$2p\pi^-$ $v = 3$ $J = 1$	105 667.64	105 671.4	105 609.1
$2p\pi^-$ $v = 2$ $J = 1$	103 627.74	103 630.0	103 567.1
$2p\pi^-$ $v = 1$ $J = 1$	101 456.33	101 457.7	101 394.2
$2p\pi^-$ $v = 0$ $J = 1$	99 150.72	99 151.2	99 086.7

[a] Assuming situation A.
[b] From Dabrowski and Herzberg, Ref. 6.
[c] Above $v = 0$, $J = 0$ of $X^1\Sigma_g^+$.
[d] Kołos and Wolniewicz, Ref. 5. These values have been obtained by subtracting from the theoretical $n = 2$ dissociation limit in the Born-Oppenheimer approximation (= 118 302.3 cm^{-1} above the theoretical $v = 0$, $J = 0$ level of $X^1\Sigma_g^+$, corrected for adiabatic and nonadiabatic effects) the values in the column "$J = 1$, $\Lambda = 0$" of Ref. 5.

the energy measured from this limit. The theoretical values (circles) lie on the curve representing $n - n^*(1)$ as a function of $T - T^+(1)$ according to Eq. (6). Obviously all levels except $n = 7$ and 11 are close to situation B, having a constant quantum defect $n - n^*(1) = \mu_{p\pi}(v = 1) = (1/\pi)\arctan M_{11}$ $= -0.087$. The levels $n = 7$ and 11 are perturbed by the members of $n = 5$ and 6, respectively, of the series converging to the next higher limit, $T^+(v = 2)(N = 1)$. These perturbations had been observed by Herzberg and Jungen,[2] who interpreted them as due to vibration-electron coupling and determined the element M_{12} by perturbation theory. The present *ab initio* calculation predicts correctly both the unperturbed levels and the perturbations. (Note that, e.g., the perturbation at $n = 11$ corresponds to an energy-level displacement of 3.5 cm^{-1}.)

Table II refers to a case close to situation A, namely to the $C^1\Pi_u^-$ state which is the lowest member of the $np\pi^-$ series. The first column lists the values observed by Dabrowski and Herzberg for $J = 1$[6]; the second and third columns give the results of our calculations and of the Born-Oppenheimer calculation of Kołos and Wolniewicz,[5] respectively. Both theoretical calculations are based on the *same* potential-energy curve, but the agreement between theory and experiment is greatly improved in our calculation. Kołos and Wolniewicz[5] assumed situation A to hold strictly and determined the level positions by solving the

vibrational Schrödinger equation for the potential (1). Since the difference between their results and the observed energies must correspond to the sum of adiabatic and nonadiabatic corrections, we can say that they are built into the quantum-defect treatment.

The calculations reported here are limited to a small range of low v values. Similar calculations involving higher v quantum numbers, or the vibrational continuum (predissociation), would require two improvements of the theory. First, at intermediate R values ($\simeq 2R_e$) strong configuration mixing occurs,[7] necessitating the inclusion of states with an excited H_2^+ core. Second, at still larger R values, the quantum number $l = 1$ of the Rydberg electron ceases to be well defined, and mixing with $l = 3, 5, \ldots$ states becomes possible.
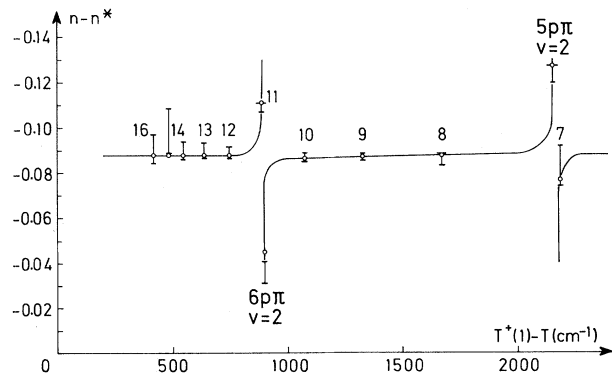
A detailed account of this work will be given

FIG. 1. Quantum-defect plot of the $np\pi^-$, $v = 1$, $J = 1$ Rydberg series of H_2.

elsewhere.[12] A similar study of the np $^1\Sigma_u^-$ excited states of H_2 is in progress, as well as an extension to the effect of predissociation and preionization on the profile of lines lying above the dissociation and ionization limits.

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Intensity Variations of K^--Mesonic X Rays*

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We show that there exists a strong correlation between the atomic diameter of target metals and their K^- mesonic x-ray intensity. The smaller x-ray intensities observed from smaller atoms suggests that the initial capture into large angular momentum states is inhibited in smaller atoms which could be understood if the meson is not localized about a single atom until its kinetic energy is somewhat less than has been presumed. This tendency for mesons to avoid higher angular momentum states when captured by small atoms also explains some previous muonic-atom results.

Recently Wiegand and Godfrey[1] have performed an encyclopedic experiment where the intensities of 346 K^--mesonic x-ray lines were measured for a variety of targets spanning the periodic table. These authors observed unexpected variations in intensities of many of the lines not expected to be influenced by nuclear absorption, even in nearby elements. For example, the intensity of the $n = 11$ to $n = 10$ transition in Au^{179} was found to be 0.16 ± 0.05 x rays per K^- stop, whereas this same transition in Bi^{209} had an intensity of 0.36 ± 0.07. Similar sharp variations in x-ray intensities for muonic atoms have been reported by Kessler *et al.*[2] and by Quitmann *et al.*[3] On the basis of available theoretical models, such intensity variations must be considered anomalous. Leon and Seki,[4] who have recently calculated the expected K^- x-ray intensities from a semiclassical model, suggest that these fluctuations derive from variations in atomic structure. While we cannot exclude this possibility, we wish to point out, that, for the metallic targets used by Wiegand and Godfrey,[1] there is a close correlation between the observed intensities and the internuclear spacing (atomic diameter) of the target material. I only consider metallic targets to avoid any effects on the kaons, cascade due to electron depletion in the mesonic atom.

In Fig. 1, I plot the observed x-ray intensities versus Z of the target element for the Group IV, V, VI metals studied by Wiegand and Godfrey.[1] For the Group IV metals the transition intensities plotted are an average of the $n = 7 \to 6$ and $n = 6 \to 5$ intensities, while for the Group V metals, I plot an average of the $n = 8 \to 7$ and $n = 7 \to 6$ intensities, and for Group VI, I use an average of the $n = 11 \to 10$ and $n = 10 \to 9$ transitions. The use of average values should tend to smooth out any individ-