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Auto-Ionization in Molecular Systems*

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When one of the electrons in a diatomic molecule is highly excited, the molecular system is, in many respects, similar to a hydrogen atom; a single electron moves in the field of a small, singly charged core. These states, called Rydberg states of the diatomic molecule, can essentially be characterized by hydrogenic quantum numbers n and l, provided that n is large enough so that the orbital radius of the Rydberg electron is large compared to the dimensions of the ion core. However, unlike the hydrogen atom, the ionic core generates not only a Coulomb field, but higher multipole potentials as well. In addition, the ionic core can be vibrationally and rotationally excited with excitation energies greater than the binding energy of the Rydberg electron. When this happens, auto-ionization can occur. This process is very similar to the nuclear internal-conversion process in which an excited nucleus, instead of emitting a γ ray, de-excites by giving up its energy directly to an atomic electron. By taking advantage of the similarity between the auto-ionization and internal-conversion processes, auto-ionization lifetimes for Rydberg states of H_2 and HD are calculated. These results are compared with experimental results and with those obtained from an alternative approach.

I. INTRODUCTION

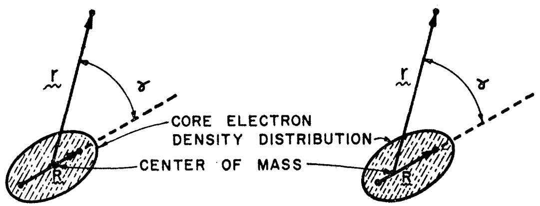
In a diatomic molecule if one electron is removed sufficiently far from the core, it essentially moves in the field of a unit charge. Thus, there exists a series of Rydberg states with energies

$$E_n \simeq -R_\infty/n^2 \tag{1}$$

for large n. However, the ionic core supplies not only a monopole potential energy $-e^2/r$, but, being an extended charge distribution, it also has higher multipole components as well. In general, it will generate a quadrupole potential that falls off as r^{-3} and, for heteronuclear cases, it will generate a dipole potential as well, which falls off as r^{-2}. In addition, since the core is polarizable there will be a polarization potential which falls off as r^{-4}. This polarization potential is produced by adiabatic distortion of the core due to the outer electron itself; the potential, in turn, acts back on the outer electron. However, in this work we will neglect the polarization effects because they fall off faster with increasing radius than do the multipole components we are considering. Referring to Fig. 1, it is clear that if one electron is excited to a Rydberg state with large n, the outer electron "sees" a small core whose principal effect is to produce the $-e^2/r$ potential energy that binds it to the core, but which contains higher multipole potentials as well.

Such a decomposition of the Born-Oppenheimer molecular Hamiltonian into core and outer electronic parts was first proposed by Berry,[1] who calculated in a first-order perturbation treatment auto-ionization rates for some $l=1$ Rydberg states. He assumed the auto-ionizing transitions to be produced by a nonadiabatic term in the exact Schrödinger equation, which breaks down the Born-Oppenheimer approximation by coupling the core vibrations and the electronic states of the outer electron. The present work differs from the approach of Berry in that it exploits the analogy of the ionic core of a molecule in a high Rydberg state with an atomic nucleus, and the analogy of the molecular auto-ionization process with the internal-conversion process of nuclear physics.

The energy difference between the ground and the first excited *electronic* state of the ionic core is large compared with the energy differences between the Rydberg levels of the outer electron for large values of n. Therefore the effect of the outer electron in determining the core structure can be neglected. On the other hand, the deviation from pure Coulombic form of the interaction potential between the ionic core and the Rydberg electron has the effect of perturbing the energy levels of non-auto-ionizing states from an exact $1/n^2$ sequence, much as an ordinary nucleus that has a



(a) HOMONUCLEAR CASE (b) HETERONUCLEAR CASE

FIG. 1. Schematic representation of a Rydberg configuration of the hydrogen molecules (a) H_2 or D_2, and (b) HD. The excited electron is located at $\mathbf{r}$ relative to the center of mass. The ionic charge consists of two positively charged hydrogen nuclei surrounded by the negative charge distribution produced by the tightly bound inner electron.

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[1] R. S. Berry, J. Chem. Phys. 45, 1228 (1966).

magnetic moment and a quadrupole moment will shift the energy levels of the corresponding atom into the various hyperfine levels. These shifts can be readily calculated although at the present time there are no experimental data accurate enough to make a meaningful comparison.

To push further the analogy of the molecular ionic core with an atomic nucleus, it may be noted that a process called internal conversion has been well documented in nuclear physics.[2] A nucleus in an excited state can, and often does, revert to the ground state by the emission of a γ ray. However, in a percentage of the cases the excited nucleus interacts directly with one of the atomic electrons (usually a $1s$ electron), gives up its excitation energy to that electron, and reverts to a lower state, while the electron is ejected with a characteristic energy.

Similarly, in a Rydberg state of a diatomic molecule, the ionic core, which serves as a nucleus, can be excited also. It can be in any one of the vibrational-rotational states characteristic of that molecular ion. When energetically allowed, the ionic core can give up some or all of its energy to the outer electron, thus reverting to a lower vibrational-rotational state. The outer electron would then be ejected with a characteristic energy, the difference between the initial and final vibrational-rotational energies of the core minus the absolute value of the original binding energy of the outer electron.

In considering the analogy between an atomic nucleus and the ionic core of a Rydberg state of a diatomic molecule, two differences must be noted.

First, the energy levels of a nucleus are considerably greater than those of the orbital electrons. Thus, in the nucleus, internal conversion is always energetically favorable. On the other hand, the vibrational-rotational states of a molecular ion are low compared with electronic binding energies in general. Thus, the process analogous to internal conversion is not always energetically allowed.

Second, the ratio of the size of the ionic core to the radius of the Bohr orbit of the outer electron is $\sim 2a_0/n^2a_0$, which is generally much larger than the analogous ratio of the radius of the nucleus to that of the $1s$-electron Bohr orbit, viz., $(5\times10^{-13}\text{ cm})/(0.5\times10^{-8}/Z\text{ cm})$. Thus, the molecular analog to internal conversion is far more likely, when the process is energetically allowed, then is the true internal-conversion process.

Two phenomena are studied in this work. The first is a series of peaks in the photo-ionization cross section measured by Diebler, Reese, and Krauss.[3] These authors were able to present only a qualitative theoretical treatment of the expected auto-ionization lifetimes in terms of conventional molecular theory. It will be seen, on the other hand, that for Rydberg states visualized in terms of the model described in the present work, quantitative results can easily be obtained. In fact, auto-ionization lifetimes were also obtained by Berry, whose model lies between the present model and that of Ref. 3. His results, when compared to those obtained in the present work, are in general agreement insofar as quasiselection rules are concerned, but differ in important details, principally in angular-momentum effects. This will be discussed more fully in Sec. IV.

The second phenomenon to be considered here is the presence of a substantial number of long-lived auto-ionizing Rydberg states observed in beam experiments by Barnett, Ray, and Langley[4] in which H_2^+ captures an electron to form H_2^* in a Rydberg state. At first glance this is surprising in view of the generally short-lived behavior of auto-ionizing states. It is even more surprising that these lifetimes are much longer than could possibly be observed in the photo-ionization experiments of Diebler, Reese, and Krauss. This fact will also be resolved by the model in terms of quasi-selection rules.

Finally, to conclude this section, it should be pointed out that although the model described by Berry and that described in this work have much in common, as will be demonstrated in Sec. IV, they do involve (insofar as the auto-ionizing states are concerned) some intrinsically different physical assumptions. These are not merely differences of calculational convenience or mathematical approximation, even apart from a difference in handling angular momentum. To understand this it must be realized that auot-ionizing states are not true eigenfunctions of the Hamiltonian for the molecular system. This point has long been understood for auto-ionization of atomic systems. As it pertains to the molecular auto-ionization process, which is the subject of this work, the fact is that the potential energy of interaction between core and outer electron, which is common to both models, cannot be used both to define the initial state and to mediate the auto-ionization transition.[5,6] On one hand, Berry uses the full potential to define the auto-ionization state and uses a kinetic vibronic coupling term in the exact Schrödinger equation to produce the auto-ionizing transition. In the present work, on the other hand, the core–Rydberg-electron potential energy common to both models is decomposed by means of projection operators into a part which determines the state and a part which mediates the auto-ionizing transition.[6] The analogy with the internal-conversion process amounts to neglecting that part of the decomposed potential which contributes to the states, thus approximating the auto-ionizing Rydberg states by pure atomic states for the outer

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[2] See, e.g., J. M. Blatt and V. F. Weisskopf, *Theoretical Nuclear Physics* (John Wiley & Sons, Inc., New York, 1952), pp. 614–622.

[3] V. H. Diebler, R. M. Reese, and M. Krauss, J. Chem. Phys. **42**, 2045 (1965).

[4] C. F. Barnett, J. A. Ray, and R. A. Langley (to be published).

[5] B. H. Bransden and A. Dalgarno, Proc. Phys. Soc. (London) **A66**, 904 (1953).

[6] L. Lipsky and A. Russek, Phys. Rev. **142**, 59 (1966).

electron multiplied by pure vibrational-rotational states of the ion core.

It must be emphasized that neither approach is intrinisically right or wrong. They start with different initial states which subsequently auto-ionize. (Remember that auto-ionizing states are merely initial states which, not being true stationary states of the total Hamiltonian for the system, alter as time unfolds. This alteration is the decay to ionized state.) Now, an initial state is entirely at the whim of the experimental situation that creates the initial state. Therefore all models for auto-ionizing states must be evaluated in light of the experimental situation. What may be a good state to describe one situation may be inappropriate in another.

If we are to account for the existence of long-lived, high Rydberg auto-ionizing states, which are observed in the capture of an electron by H_2^+, then we are forced to the model presented in this paper. For many of the states found by Diebler, Reese, and Krauss, on the other hand, the model might well be inappropriate.

II. MATHEMATICAL FORMULATION

If an electron in a diatomic molecule is highly excited, the main force that acts on it is the Coulomb force due to the residual unit charge on the ionic core. For its part, the core structure is virtually undisturbed by the slowly moving outer electron. Thus, to a good approximation, the Hamiltonian for the system can be taken to be

$$H(\mathbf{r},\mathbf{R})=H_c(\mathbf{R})+H_e(\mathbf{r})+V(\mathbf{R},\mathbf{r}). \tag{2}$$

Here $H_c(\mathbf{R})$ is the core Hamiltonian in the Born-Oppenheimer approximation,

$$H_c(\mathbf{R})=\frac{P^2}{2M}+\frac{Z_1Z_2e^2}{R}+E_e(R), \tag{3}$$

where $E_e(R)$ is the electronic energy of the core only, in the Born-Oppenheimer approximation, and M is the reduced mass of the two nuclei;

$$H_e(\mathbf{r})=\frac{p^2}{2m}-\frac{e^2}{r}, \tag{4}$$

and

$$V(\mathbf{R},\mathbf{r})=-\frac{D(R)}{r^2}\cos\gamma-\frac{Q(R)}{r^3}[\tfrac{3}{2}\cos^2\gamma-\tfrac{1}{2}], \quad r\gg R. \tag{5}$$

Thus, only the monopole term in the potential produced by the core has been incorporated into the unperturbed Hamiltonian of the outer electron, because it is by far the most important in determining the motion of the electron. The solutions of (4) are well known and, fortunately, are independent of the nuclear separation R. Whereas in Berry's approach $V(\mathbf{R},\mathbf{r})$ is included in $H_e(\mathbf{r})$, in the present work $V(\mathbf{R},\mathbf{r})$ is considered to constitute the perturbation term in the Hamiltonian, which shifts energy levels slightly and is responsible for the auto-ionization transition in auto-ionizing states. The angle γ is, as shown in Fig. 1, the angle between the electronic position vector $\mathbf{r}$ and the internuclear separation vector $\mathbf{R}$:

$$\cos\gamma=\mathbf{r}\cdot\mathbf{R}/rR. \tag{6}$$

The origin, with respect to which the electronic coordinates are measured, is taken to be the center of mass of the ionic core, since the electronic mass can be neglected when compared with that of the ionic core and therefore has a negligible effect on the over-all center of mass. The quantities $D(R)$ and $Q(R)$ are the electronic charge e (>0) times, respectively, the core electric-dipole and electric-quadrupole moment, calculated in the Born-Oppenheimer approximation when the instantaneous nuclear separation is R.

It is to be noted that the core electron is taken into account only through its effect on the core vibrational and rotational motion in the Born-Oppenheimer approximation and through its contribution to the core dipole and quadrupole moments. The electronic structure of the core is treated as being entirely uncoupled from the outer electron. This is justified on the basis that the outer electron moves very slowly compared with the core electron and therefore "sees" only the average charge distribution created by the core electronic structure. The lowest-order interaction of the outer electron with the core electronic structure would be via the polarization potential which falls off as r^{-4} and is being neglected here. An additional effect of the core electron which is being neglected is that which operates via the exclusion principle. This effect is very small when one electron is primarily close to the origin while the other is primarily far away, but it is clear that the method would break down if applied to the radiative decay of a high Rydberg state down to the ground molecular state.

Finally, it must be stressed that the interaction term defined by Eq. (5) is an approximation valid for large r only. When $r\lesssim R$ the outer electron is penetrating the core and the actual interaction V does not become singular. Thus, in what follows, all results must be checked to ascertain that only a negligible contribution comes from the region $r\lesssim R$ where the multipole approximation to V breaks down. Otherwise, the results must be corrected for this "penetration" effect.

In working out the details of the model a distinction in principle must be made between ordinary stationary states and auto-ionizing states. The former will be briefly discussed in Sec. II A below, while the latter will be treated in Sec. II B.

A. Non-Auto-Ionizing States

The non-auto-ionizing states can be obtained using conventional perturbation theory. The Hamiltonian for the over-all molecular system can be decomposed into two parts:

$$H=H_{\mathrm{NI}}+V\,, \tag{7}$$

where V is given by Eq. (5) and

$$H_{\mathrm{NI}}=H_c(\mathbf{R})+H_e(\mathbf{r})\,. \tag{8}$$

The unperturbed Hamiltonian H_{NI} consists of two uncoupled terms (NI stands for "noninteracting") so that an eigenfunction of H_{NI} is simply a product of an eigenfunction of H_c and an eigenfunction of H_e, each of which can be written as a product of a radial function times an angular factor. Assuming that the core electron is in the $1s\sigma_g$ state, the eigenfunctions of H_{NI} take the form (see the Appendix)

$$\Psi_{\nu\lambda\mu nlm}(\mathbf{R},\mathbf{r})=F_{\nu\lambda}(R)Y_\lambda{}^\mu(\Theta,\Phi)R_{nl}(r)Y_l{}^m(\theta,\varphi)\,. \tag{9}$$

The wave function Ψ given by (9) describes a state of H_{NI} wherein the ionic core is the νth vibrational state and λth rotational state with projection μ on the laboratory z axis, while the outer electron is in the nth Rydberg level with angular momentum l and projection m. The unperturbed energy $E^{(0)}$ associated with this state is, in atomic units,

$$E_{\nu\lambda n}{}^{(0)}=\epsilon_{\nu\lambda}-1/2n^2\,, \tag{10a}$$

where $\epsilon_{\nu\lambda}$ is the vibrational-rotational energy of the ionic core. This can be further approximated as

$$E_{\nu\lambda n}{}^{(0)}=\epsilon_\nu+\lambda(\lambda+1)/2\mathcal{I}_\nu-1/2n^2 \tag{10b}$$

if the coupling of the rotational motion to the vibrational motion is ignored. Clearly this level is degenerate with respect to the azimuthal quantum numbers μ and m. Consequently, the actual states for which total angular momentum J and its projection M on the laboratory z axis are constants of the motion will be linear combinations of these degenerate levels, the coefficients being the ordinary Clebsch-Gordan coefficients. Thus,

$$\Psi_{\nu\lambda nlJM}=F_{\nu\lambda}(R)R_{nl}(r)\sum C_{\lambda l;\,JM}{}^{\mu m}\times Y_\lambda{}^\mu(\Theta,\Phi)Y_l{}^m(\theta,\varphi)\,. \tag{11}$$

For those non-auto-ionizing states, the first-order correction to the energy level given by (10) is given by

$$\begin{aligned}\Delta E=&-\langle F_{\nu\lambda}|D(R)|F_{\nu\lambda}\rangle\langle R_{nl}|1/r^2|R_{nl}\rangle\\&\times\sum_{m\mu}\sum_{m'\mu'}C_{\lambda l;\,JM}{}^{\mu m}C_{\lambda l;\,JM}{}^{\mu' m'}\\&\times\langle Y_\lambda{}^\mu Y_l{}^m|P_1(\cos\gamma)|Y_\lambda{}^{\mu'}Y_l{}^{m'}\rangle-\langle F_{\nu\lambda}|Q(R)|F_{\nu\lambda}\rangle\\&\times\langle R_{nl}|1/r^3|R_{nl}\rangle\sum_{m\mu}\sum_{m'\mu'}C_{\lambda l;\,JM}{}^{\mu m}C_{\lambda l;\,JM}{}^{\mu' m'}\\&\times\langle Y_\lambda{}^\mu Y_l{}^m|P_2\,(\cos\gamma)|Y_\lambda{}^{\mu'}Y_l{}^{m'}\rangle\,.\end{aligned} \tag{12}$$

However, it must be recognized that because the rotational energy is small and because the hydrogenic levels are degenerate with respect to l, a near degeneracy between levels with the same values of n and ν but different values of l and λ may make nondegenerate perturbation theory inapplicable and require a diagonalization of H with respect to the nearly degenerate states. Inasmuch as the energy levels of high Rydberg states have not experimentally been determined with sufficient accuracy to warrant the calculation of small corrections, no further attention will be devoted to this aspect.

B. Auto-Ionization Transition Rates

Inasmuch as auto-ionizing states are *not* eigenfunctions of the molecular Hamiltonian (if they were, they would never auto-ionize), care must be taken in the calculation of auto-ionization transition rates that any term in the Hamiltonian used to define the auto-ionizing state must not also be used to calculate the auto-ionization transition rate, and vice versa. Only a part of the potential V, given by Eq. (5), is responsible for the structure of the auto-ionizing state, while the remaining part mediates the auto-ionization transition. Such a decomposition of V into two complementary parts can be effected by means of Feshbach projection operators.[7,8] A treatment of atomic auto-ionizing states by this technique has already proved successful[6] and the extension to a molecular system is straightforward.

The two Fesbach projection operators are denoted by P and Q, respectively, and satisfy the relations

$$P+Q=1\,,\quad PQ=0\,,\quad P^2=P\,,\quad Q^2=Q\,. \tag{13}$$

The first two relations in (13) express the fact that P and Q are complementary. The second pair of relations express the idempotency characteristic of any projection operator. One of these operators (by convention P) projects onto that subspace of Hilbert space which contains all functions having the asymptotic behavior of the ionized state.[8,6] In the present context, a reasonable decomposition of V can be achieved by defining Q in terms of a finite basis set of functions of the form (11), which are eigenfunctions of H_{NI}. Thus,

$$Q={\sum}_\alpha{}'|\Psi_\alpha\rangle\langle\Psi_\alpha|\,,\quad P=1-Q\,, \tag{14}$$

where α stands for an entire set of quantum numbers ν, λ, n, l, J, M, and the prime on the summation means that only those molecular product states (11) are to be included in the summation which are in the selected basis set. The projection operators are clearly not unique. They are completely specified only when the basis set is. A reasonable choice of basis set, selected on grounds of physical intuition, will yield a good approximation to the auto-ionizing level. The final expression for the auto-ionization level (which is unique) is given in the formalism[6,8] as the diagonalization energy plus a small energy shift, which can be specified only when the collision process which gives rise to this state is specified

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[7] H. Feshbach, Ann. Phys. (N. Y.) **5**, 357 (1958); **19**, 287 (1962).

[8] T. F. O'Malley and S. Geltman, Phys. Rev. **137**, A1344 (1965).

in detail. The auto-ionization level is by definition a resonance in the scattering process giving rise to the state. Thus, to the extent that we are willing to discuss the auto-ionization level independently of the excitation mechanism, the energy of the auto-ionization state is indeterminate by a small amount; hence the ambiguity in the definition of the basis set and the reliance on physical intuition.

With the operators P and Q, V is decomposed into two parts: $PVP+QVQ$ which is included in the unperturbed Hamiltonian H_0, while the remainder $PVQ+QVP$ constitutes the perturbation term responsible for the auto-ionization transition.

$$H_0=H_{\mathrm{NI}}+PVP+QVQ=H_c(\mathbf{R})+H_e(\mathbf{r})+PVP+QVQ,$$
$$H'=PVQ+QVP. \tag{15}$$

The auto-ionizing states are by definition the eigenfunctions of H_0 which lie in Q space. Such an auto-ionizing state Ψ can be represented as a linear combination of the basis elements,

$$\Psi=\sum_\alpha{}'a_\alpha\Psi_\alpha. \tag{16}$$

The coefficients a_α which make Ψ an eigenfunction of H_0 are determined by the equations (see Ref. 6 for a more detailed derivation)

$$H_0\Psi=(H_{\mathrm{NI}}+PVP+QVQ)\sum_\beta{}'a_\beta\Psi_\beta=E\sum_\alpha{}'a_\alpha\Psi_\alpha,$$

which reduces to

$$\sum_\alpha{}'\sum_\beta{}'\,a_\beta\langle\Psi_\alpha|H_{\mathrm{NI}}+V|\Psi_\beta\rangle\Psi_\alpha=E\sum_\alpha{}'\,a_\alpha\Psi_\alpha.$$

Equating coefficients of Ψ_α yields

$$\sum_\beta{}'\,a_\beta\langle\Psi_\alpha|H_{\mathrm{NI}}+V|\Psi_\beta\rangle=Ea_\alpha. \tag{17}$$

In deriving (17), Eq. (14) and the following relations were used:

$$P\Psi_\alpha=0,\quad Q\Psi_\alpha=\Psi_\alpha\quad\text{if}\quad\Psi_\alpha\text{ in basis set}. \tag{18}$$

Remembering that Ψ_β is an eigenfunction of H_{NI} belonging to the eigenvalue $E_\beta^{(0)}$, Eqs. (17) for the coefficients can be rewritten:

$$\sum_\beta{}'\,a_\beta[(E_\alpha^{(0)}-E)\delta_{\alpha\beta}+V_{\alpha\beta}]=0. \tag{19}$$

From (17) it is clear that the auto-ionizing state is determined by diagonalizing the submatrix $H_{\alpha\beta}$, where α and β lie in the finite dimensional subspace which determines Q space.

In principle, when dealing with the nuclear internal-conversion process the atomic states should be modified according to the prescription described above. In practice, however, this is never done. On *a priori* grounds it is reasoned that the configuration mixing induced by the extra terms PVP and QVQ is negligible, so that the raw eigenstates of H_{NI} can be used to a very high degree of approximation. In the molecular analog under consideration this approximation is complicated by the near degeneracy of some of the states involved, which could cause considerable mixing of these states. However, off-diagonal matrix elements of QVQ between these nearly degenerate states vanish, so that there is in fact no mixing.[9] With this approximation, and provided that the unbound electron wave functions are normalized according to the prescription

$$\langle\varphi_{kl}|\varphi_{k'l'}\rangle=\delta_{ll'}\delta(E_k-E_{k'}), \tag{20}$$

then the auto-ionization transition rate per unit time w is given by

$$w=\frac{2\pi}{\hbar}|\langle\nu\lambda nlJM|V|\nu'\lambda'k'l'JM\rangle|^2. \tag{21a}$$

Here

$$\begin{aligned}\langle\nu\lambda nlJM|V|\nu'\lambda'k'l'JM\rangle\\ =-\langle F_{\nu\lambda}|D(R)|F_{\nu'\lambda'}\rangle\langle R_{nl}|1/r^2|R_{k'l'}\rangle\\ \times\sum_{\mu m}\sum_{\mu'm'}C_{\lambda l;\,JM}{}^{\mu m}C_{\lambda'l';\,JM}{}^{\mu'm'}\\ \times\langle Y_\lambda{}^\mu Y_l{}^m|P_1(\cos\gamma)|Y_{\lambda'}{}^{\mu'}Y_{l'}{}^{m'}\rangle\\ -\langle F_{\nu\lambda}|Q(R)|F_{\nu'\lambda'}\rangle\langle R_{nl}|1/r^3|R_{k'l'}\rangle\\ \times\sum_{\mu m}\sum_{\mu'm'}C_{\lambda l;\,JM}{}^{\mu m}C_{\lambda'l';\,JM}{}^{\mu'm'}\\ \times\langle Y_\lambda{}^\mu Y_l{}^m|P_2(\cos\gamma)|Y_{\lambda'}{}^{\mu'}Y_{l'}{}^{m'}\rangle.\end{aligned} \tag{21b}$$

This expression looks unwieldy, but it is quite tractable and quantitative calculations have been carried out. The factors appearing in Eqs. (21) are tabulated in Tables I–III for several representative values of ν, λ, ν', λ' and n, l, l'. Since all ejected electrons here considered will be ejected with $k'\ll 1$ in atomic units (a.u.), k' has been set equal to zero for simplicity in the calculations. The radial functions for the outer electron both bound and unbound were obtained from Landau and Lifshitz's text.[10] The unbound electron of zero energy, normalized on the energy scale, is given by Landau and Lifshitz as

$$R_{0l}=(2/r)^{1/2}J_{2l+1}((8r)^{1/2}).$$

Berry[1] has estimated that approximately 30% of the electronic integral comes from the region $r\leq 1$ a.u., 30% comes from the region $1\leq r\leq 2$ a.u., and the remainder from the region $2\leq r\leq\infty$. The electronic factors in the matrix elements are, therefore, not particularly accurate, but they should, as Berry concludes, be correct to within a factor of 2.

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[9] There appears to be an identity involving Laguerre polynomials such that for hydrogenic functions $\langle R_{nl'}|1/r^{l+1}|R_{n,l+l'}\rangle=0$. Note that this integral involves hydrogenic radial functions with the same n but different l. It has not been possible at present to establish this identity in complete generality, but the result has been directly verified for all cases that arise in this paper. This identity does not insure the vanishing of all off-diagonal matrix elements between states with the same value of n. The remainder vanish because of the angular integrals.

[10] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1958), Sec. 36.

TABLE I. Sample dipole and quadrupole core matrix elements for HD^+.

ν	λ	ν'	λ'	$\langle F_{\nu\lambda} \vert D(R) \vert F_{\nu'\lambda'} \rangle$	$\langle F_{\nu\lambda} \vert Q(R) \vert F_{\nu'\lambda'} \rangle$
1	0	0	0	−0.035	−0.341
1	1	0	0	−0.034	−0.333
2	1	0	0	−0.004	−0.025
3	1	0	0	0.000	−0.003
5	1	0	0	0.000	0.000
9	1	0	0	0.000	0.000
1	1	0	1	−0.035	−0.342
2	1	0	1	−0.004	−0.024
3	1	0	1	0.000	−0.003
5	1	0	1	0.000	0.000
9	1	0	1	0.000	0.000

The quantity $D(R)$ is given by

$$D(R)=eP_{\mathbf{R}}(R),$$

where $P_{\mathbf{R}}(R)$ is the dipole moment of the core with respect to the center of mass, which has contributions from the nuclear center of charge in HD^+. The dipole moment is just the distance from the charge center to the center of mass times the total electric charge of the core, $+e$. Hence

$$D(R)=e^2\left(\frac{f_2-f_1}{2}\right)R,$$

where the body-fixed Z axis is directed along $\mathbf{R}$ from nucleus 2 to nucleus 1 and

$$f_i=m_i/(m_1+m_2),\quad i=1,2.$$

The quantity $Q(R)$ in Eq. (5) is defined by

$$Q(R)=eQ_{\mathbf{RR}}(R),$$

where $Q_{\mathbf{RR}}(R)$ is the component of the quadrupole moment, produced by the core electron and nuclei, defined by

$$Q_{\mathbf{RR}}(R)=-\tfrac{1}{2}e\int(3z_c{}^2-r_c{}^2)\vert\psi_{1s\sigma_g}(R,\xi,\eta)\vert^2d^3r_c +\tfrac{1}{2}e[2f_2{}^2R^2+2f_1{}^2R^2].$$

TABLE II. Sample quadrupole core matrix elements for H_2^+.

ν	λ	ν'	λ	$\langle F_{\nu\lambda} \vert Q(R) \vert F_{\nu'\lambda'} \rangle$
1	2	0	0	−0.3136
2	2	0	0	−0.0289
3	2	0	0	−0.0047
5	2	0	0	0.0000
9	2	0	0	0.0000
1	1	0	1	−0.3431
2	1	0	1	−0.0263
3	1	0	1	−0.0037
5	1	0	1	0.0000
1	2	0	2	−0.3442
2	2	0	2	−0.0265
3	2	0	2	−0.0037
5	2	0	2	0.0000

The coordinates z_c and r_c of the core electron relative to the nuclear center of mass can be expressed in terms of prolate spheroidal coordinates by

$$z_c=-\tfrac{1}{2}R[\xi\eta+(f_1-f_2)],$$
$$r_c=\tfrac{1}{2}R[\xi^2+\eta^2-1+2(f_1-f_2)\xi\eta+(f_1-f_2)^2]^{1/2}.$$

Then one obtains for the homonuclear case ($f_1=f_2=\frac{1}{2}$),

$$Q_{\mathrm{homo}}(R)=-\tfrac{1}{8}e^2R^2\left\{1+\int d^3r_c[3\xi^2\eta^2-\xi^2-\eta^2] \times\vert\psi_{1s\sigma g}(R,\xi,\eta)\vert^2\right\}+\tfrac{1}{2}e^2R^2.$$

In the heteronuclear case (HD^+) the electronic contribution is altered by $-\frac{1}{4}e^2R^2(f_2-f_1)^2$ and the nuclear contribution by $+\frac{1}{2}e^2R^2(f_2-f_1)^2$ because of the change of origin, so that

$$Q_{\mathrm{het}}(R)=Q_{\mathrm{homo}}(R)+\tfrac{1}{4}e^2R^2(f_2-f_1)^2.$$

TABLE III. Sample dipole and quadrupole electronic radial integrals.

n	l	l'	$\langle R_{nl} \vert 1/r^2 \vert R_{kl'} \rangle \vert_{k=0}$	$\langle R_{nl} \vert 1/r^3 \vert R_{kl'} \rangle \vert_{k=0}$
3	1	1	0.0973	0.0621
6	1	1	0.0387	0.0225
8	1	1	0.0259	0.0147
10	1	1	0.0189	0.0105
3	1	0	0.0162	[a]
6	1	0	0.00468	[a]
8	1	0	0.00269	[a]
10	1	0	0.00174	[a]
3	2	2		0.0100
6	2	2		0.0044
8	2	2		0.0029
10	2	2		0.0021
6	0	1	0.00812	[a]
8	0	1	0.00422	[a]
10	0	1	0.00255	[a]
14	0	1	0.00120	[a]
6	0	2	[a]	−0.00029
8	0	2	[a]	−0.00012
10	0	2	[a]	−0.00006
14	0	2	[a]	−0.00002

[a] Transition forbidden by angular-momentum selection rules.

The contributions of the core electron to $D(R)$ and $Q(R)$ were calculated with the exact two-center $1s\sigma_g$ wave function[11] using Legendre-Gauss quadrature over η and a combination of Legendre-Gauss and Laguerre-Gauss integration over ξ. The adiabatic vibrational wave functions used in computing the matrix elements $\langle F_{\nu\lambda}\vert D(R)\vert F_{\nu'\lambda'}\rangle$ and $\langle F_{\nu\lambda}\vert Q(R)\vert F_{\nu'\lambda'}\rangle$ were those of Patterson and Becker.[12] In the homonuclear case the vibrational equation included the lowest-order diagonal correction[13] to the Born-Oppenheimer approximation calculated from the exact two-center $1s\sigma_g$ electronic function in Ref. 12. In the heteronuclear case, the Born-

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[11] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London **A246**, 215 (1953).

[12] M. R. Patterson and R. L. Becker, Oak Ridge National Laboratory Report No. ORNL-TM-1850, 1967 (unpublished).

[13] See, e.g., S. Cohen, D. L. Judd, and R. J. Riddell, Jr., Phys. Rev. **119**, 384 (1960). The correction term is denoted by $g_{++}(R)$.

Oppenheimer approximation was used without correction. The vibrational matrix elements were calculated using Newton-Coates quadrature. The homonuclear matrix elements are estimated to be accurate to within ± 0.0004, but the heteronuclear ones only to within ± 0.004.

III. RESULTS

Tables I–III constitute only a small sample of a virtually undigestible mass of results. In order to make them useful, it is necessary to distill from these results certain quasiselection rules. Bearing in mind that all probabilities are formed from the square of the matrix element, then it can be seen from Tables I and II that:

(1) Any transition is unlikely unless the vibrational quantum number decreases by 1: $\nu_I-\nu_F=1$. Transitions in which ν decreases by 2 have lifetimes 100 or more times longer than those for which ν decreases by 1.

(2) In general, the transition rate is unaffected by change of angular momentum of the ion core.

(3) Similarly, it can be seen from Table III that any transition is unlikely unless the electronic angular momentum is unchanged: $\Delta l=0$. An exception to this rule is that the 0-0 transition is always expressly forbidden [by angular integrals in Eq. (21b)], and for those cases in which the core dipole moment is zero, 0-1 transitions are also forbidden.

Despite differences in the actual values obtained in this work and those obtained by Berry, these qualitative features are common to both works. Values for auto-ionization lifetimes are presented in Tables IV and V for two different sets of states which are important in the discussion of two different types of experimental effects.

A. Auto-Ionization Effects in Photo-Ionization

A series of peaks in the photo-ionization cross sections of H_2, D_2, and HD obtained by Diebler, Reese, and Krauss[3] has been attributed to excitation of auto-ionization states. These auto-ionizing states are unquestionably $l=1$ states because of the very strong selection rules that hold for processes involving absorption or emission of photons. Further, because of the relatively strong quasiselection rule 3 that holds for auto-ionizing transitions, the only final state that need be considered is that in which the emitted electron also has $l=1$. With these restrictions imposed by the experimental situation, there are only a manageable number of cases which need to be considered. Since parity considerations forbid a transition with no change in orbital angular momentum of the Rydberg electron to be mediated by the dipole term, only the quadrupole term is effective. To further limit the number of cases, only core transitions $\lambda=1$ to $\lambda'=1$ will be considered, inasmuch as 0-0 and 0-1 transitions are forbidden by the angular integrals in the quadrupole term in the matrix element. The auto-ionization transitions are obtained from Eqs. (21) using Tables I–III and are listed in Table IV.

TABLE IV. Representative transition rates for auto-ionizing Rydberg states of H_2^* in $l=1$ states.

n_i	l_i	l_f	Transition rate (sec^{-1})	$\nu_i-\nu_f$ [a]
6	1	1	1.41×10^{8}	2
7	1	1	1.64×10^{10}	1
8	1	1	1.02×10^{10}	1
10	1	1	0.52×10^{10}	1

[a] In all cases the smallest change of vibrational state that can supply the requisite energy needed for auto-ionization is used.

The transition rates, as shown in Table IV, are of the order of 10^{10} sec^{-1} provided that the Rydberg electron has $n\geq 7$ so that it can auto-ionize when the core vibrational state decreases by one. (An $n=7$ electron requires at least 0.277 eV to auto-ionize. The $\nu=1$ to $\nu=0$ transition in the H_2^+ core supplies 0.28 eV, which is just barely above the threshold.) These transition rates are considerably smaller than those reported by Berry, who obtains rates of 10^{13} sec^{-1}. The discrepancy is partially due to core angular-momentum considerations, which Berry neglects. It will be noted from Eq. (21b) that the quadrupole matrix element forbids a $\lambda=0$ to $\lambda'=0$ transition. On the other hand, Berry restricts his consideration to the 0-0 core transition (i.e., a fixed internuclear axis), neglecting angular-momentum conservation. Were we to replace the angular factor of Eq. (21b) by $\langle Y_l^m(\theta,\varphi)|P_2(\cos\theta)\times|Y_{l'}^{m'}(\theta,\varphi)\rangle$ and drop the Clebsch-Gordan coefficients coupling the core to the outer electron, we would pick up a factor 5 in the matrix element. Thus our results would increase (incorrectly) by a factor of 25 in the transition rate. This would yield transition rates of the order of 10^{11} transitions/sec. The remaining discrepancy that is not ascribable to core angular-momentum considerations is not nearly so important as the difference in behavior of the transition rate for increasing n. In Berry's calculation they increase drastically for increasing n. In this work, the matrix elements are found to decrease with increasing n. Recently Bardsley[14] has derived, from rather general considerations, the behavior

TABLE V. Representative transition rates for auto-ionizing Rydberg $l=0$ states.

n_i	l_i	ν_i	l_f	ν_f	Molecule	Transition rate (sec^{-1})
7	0	1	1	0	HD	12.15×10^{8}
8	0	1	1	0	HD	5.68×10^{8}
10	0	1	1	0	HD	2.08×10^{8}
14	0	1	1	0	HD	0.46×10^{8}
7	0	1	2	0	H_2	4.33×10^{7}
8	0	1	2	0	H_2	1.42×10^{7}
10	0	1	2	0	H_2	0.37×10^{7}
14	0	1	2	0	H_2	0.04×10^{7}

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[14] J. N. Bardsley, Chem. Phys. Letters **1**, 229 (1967).

of the transition rate as a function of n. He also obtains a decreasing of the transition rate with increasing n.

Despite the substantial differences in the lifetimes reported by Berry and those reported here, the conclusions, insofar as they apply to the data of Diebler, Reese, and Krauss, remain unchanged. High Rydberg states will auto-ionize before radiative de-excitation. These high Rydberg auto-ionizing states offer an explanation for some of the observed peaks. In H_2, D_2, and HD, a series of peaks in the photo-ionization cross section is found at the *vibrational levels of the ionized molecule* (i.e. at the ionization energy of the molecule plus the vibrational energy of the ion core). This is especially apparent in the case of HD. These peaks can be qualitatively understood as follows:

When an electron is removed to a high Rydberg state by the incident photon, the effective electronic energy of the ion core, in the Born-Oppenheimer approximation, changes suddenly. Thus, insofar as the ion core is concerned, its "spring constant" changes suddenly. Consequently, the ion core will be left, with varying probabilities, in the various vibrational states of the ion core system. (It is a favorite problem, in elementary quantum mechanics courses, to calculate the probability that a harmonic oscillator is excited to a given state of the new Hamiltonian if the spring constant is suddenly altered.) Naturally, all the energy for the total excitation comes from the incident photon. This energy is the sum of the vibrational energy of the ion core plus the excitation energy of the Rydberg electron (which, for high n, is essentially the ionization energy).

B. Long-Lived Auto-Ionizing States

A second type of experimental situation which merits study is the existence of long-lived high Rydberg auto-ionizing states. These have been observed in experiments by Barnett, Ray, and Langley[4] in which beams of H_2^+, D_2^+, and HD^+ are neutralized by electron capture. Clearly a long-lived state indicates the violation of some selection rule. Since these states have high $n(n\geq 11)$, they require very little core energy to ionize and unit change in the vibrational quantum number of the core is more than adequate. Thus, the violation does not come from the core vibrational selection rule. It comes from the angular-momentum selection rules in which the 0-0 transition is expressly forbidden in all three species and the 0-1 transition is also forbidden in H_2 and D_2, the ion cores of which have dipole moment zero.

Consequently, whenever one of these molecular ions picks up a Rydberg electron in an $l=0$ state (and this is the most common occurrence) it is forced to ionize via the much slower $\Delta l=1$ or $\Delta l=2$ transitions. Representative transition rates for these transitions are shown in Table V. It is clear from this table that $l=0$ states should be clearly seen in beam experiments in H_2 and can show up in HD experiments.

IV. COMPARISON OF MODELS

In this section the model presented in this work will be compared with that of Berry. On the surface the two models appear to have nothing in common beyond a multipole expansion of the core–Rydberg-electron potential. Berry calculates his interaction matrix element by looking into terms violating the Born-Oppenheimer approximation, whereas the model of this paper exploits the internal-conversion mechanism. Nevertheless, both models are very similar, differing mainly in details of approximation and in higher-order terms neglected in both works. The principal difference in the computational results stems only from core angular-momentum effects which can certainly be encompassed in Berry's model, but have not yet been included in his computations.

The comparison between the two models will be made using Berry's notation insofar as is convenient. For the sake of notational explicitness, the comparison will be made for quadrupole transitions, but the result is general and holds for dipole matrix elements as well.

First an identity will be established. It is from this identity that the common features will be made evident. Let $\chi_i(R)$ and $\chi_f(R)$ represent initial and final core vibrational states in the Born-Oppenheimer approximation. They satisfy a Schrödinger equation of the form

$$(P_R^2/2M)\chi(R)+V_c(R)\chi(R)=E\chi(R)\,, \qquad (22)$$

where P_R is the core vibrational momentum, $V_c(R)$ is the core potential energy including the core-electron contribution in the Born-Oppenheimer approximation, M is the reduced mass of the two nuclei, and E is the core vibrational energy. Defining the quantity I to be

$$I=\langle\chi_f(R)\,|\,Q(R)\,|\,(P_R^2/2M)\chi_i(R)\rangle_R \\ -\langle(P_R^2/2M)\chi_f(R)\,|\,Q(R)\,|\,\chi_i(R)\rangle_R\,, \qquad (23)$$

where the subscript R after the inner products denotes that these are inner products over core coordinates only, then it is simple, using Eq. (22), to verify that

$$I=(E_i-E_f)\langle\chi_f|Q|\chi_i\rangle_R\,. \qquad (24)$$

The terms involving V_c cancel each other out. On the other hand, using the fact that P_R is Hermitian, the second term in I can be rewritten

$$(2M)^{-1}\langle P_R^2\chi_f|Q|\chi_i\rangle_R=(2M)^{-1}\{\langle\chi_f|Q|P_R^2\chi_i\rangle_R \\ +2\langle\chi_f|\,(P_RQ)\,|P_R\chi_i\rangle_R+\langle\chi_f|\,(P_R^2Q)\,|\chi_i\rangle_R\}\,, \qquad (25)$$

where the parentheses indicate that the derivative operations implied by P_R are to be applied only to the quantity within the parentheses. Now the first term on the right-hand side of Eq. (25) cancels off the first term on the right-hand side of (23). Thus, we have shown that

$$(E_i-E_f)\langle\chi_f|Q|\chi_i\rangle_R=I=\frac{1}{2M}\left\{2\left\langle\chi_f\left|\left(\frac{\hbar}{i}\frac{dQ}{dR}\right)\right|\frac{\hbar}{i}\frac{d\chi_i}{dR}\right\rangle_R\right.$$

$$\left.-\left\langle\chi_f\left|\left(\hbar^2\frac{d^2Q}{dR^2}\right)\right|\chi_i\right\rangle_R\right\}. \quad (26)$$

Writing

$$\mathcal{E}_{if}=E_i-E_f\,, \quad (27a)$$

$$\mathcal{g}^{(3)}=\langle R_{k'l'}|1/r^3|R_{nl}\rangle_r\,, \quad (27b)$$

and dividing (26) through by (27a) while multiplying by (27b) yields

$$\langle R_{k'l'}|1/r^3|R_{nl}\rangle_r\langle\chi_f|Q|\chi_i\rangle_R$$

$$=\frac{1}{2M}\left\{2\left\langle\chi_f(R)\left|\frac{\mathcal{g}^{(3)}}{\mathcal{E}_{if}}\frac{\hbar}{i}\left(\frac{dQ}{dR}\right)\right|\frac{\hbar}{i}\frac{d\chi_i}{dR}\right\rangle_R\right.$$

$$\left.-\left\langle\chi_f\left|\frac{\mathcal{g}^{(3)}}{\mathcal{E}_{if}}\left(\frac{d^2Q}{dR^2}\right)\right|\chi_i\right\rangle_R\right\}. \quad (28)$$

Equation (28) forms the basis for the comparison of the two models. On the left-hand side of Eq. (28) are the core- and outer-electron integrals that appear in Eq. (21b) for our matrix elements. On the other hand, the right-hand side of Eq. (28) forms the backbone of Berry's matrix element [see his Eqs. (14) and (15)]. This takes into account not only the term T_1 [his Eq. (13a)], but also T_2 [his Eq. (13b)] which he neglects. [A factor 2 seems to have been overlooked in Berry's Eq. (13a)].

Thus we have demonstrated that whether one adopts the point of view that auto-ionization stems from terms neglected in the Born-Oppenheimer approximation or proceeds via the internal-conversion mechanism, the basic results will be the same. The most important difference between Berry's calculation and ours is that he replaces $\cos\gamma$ (where γ is the angle between the core axis and the radius vector to the Rydberg electron) by $\cos\theta$, thereby losing core recoil effects.

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APPENDIX

The total spatial wave function for a hydrogen molecular ionic core (H_2^+, D_2^+, or HD^+) can be written[15]

$$\Psi_{\nu\lambda\mu}{}^{\text{core}}(\Phi,\Theta,\phi;R,\xi,\eta)$$

$$=\sum_{\kappa=-\lambda}^{\lambda}(-)^{\mu-\kappa}D_{\mu,\kappa}{}^{\lambda}(\Phi,\Theta,\phi)G_\kappa{}^{(\nu)\lambda}(R,\xi,\eta)\,,$$

where Θ and Φ are the polar and azimuthal angles of the internuclear position vector $\mathbf{R}$; ϕ is the azimuthal angle of the core electron in the body-fixed coordinate frame; η and ξ are the prolate spheroidal coordinates of the core electron,

$$\xi=(r_{c1}+r_{c2})/R\,,\quad \eta=(r_{c1}-r_{c2})/R\,,$$

with r_{c1} and r_{c2} the distances of the electron from nuclei 1 and 2, respectively; κ is the magnetic quantum number along the figure axis (body-fixed Z axis), and $D_{\mu,\kappa}{}^{\lambda}$ is a rotation matrix element. The internal wave functions $G_\kappa{}^{\lambda}(R,\xi,\eta)$ can be expanded[12] in products of exact two-center electronic functions $\psi_i=N_i(R)\Lambda_i(\xi,R)M_i(\eta,R)$ and vibrational functions $\chi_i{}^{\lambda\nu}(R)$ with $i=(n,l,\kappa)$ in the united atom designation. In the Born-Oppenheimer approximation with the core electron in its lowest electronic state, $1s\sigma_g$, only $\kappa=0$ can occur and the core wave function becomes

$$\Psi_{\nu\lambda\mu}{}^{\text{core}}=Y_\lambda{}^{\mu}(\Theta,\Phi)F_{\nu\lambda}(R)\psi_{1s\sigma_g}(R,\xi,\eta)\,,$$

where

$$F_{\nu\lambda}(R)=\chi_{1s\sigma_g}{}^{\nu\lambda}(R)\,.$$

The core electronic function $\psi_{1s\sigma_g}$ is suppressed in writing the model wave function $\psi_{\nu\lambda\mu nlm}$, Eq. (9), for the core-plus-outer-electron system. The dipole and quadrupole moments of the core must, however, be calculated using this electronic wave function.

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[15] E. P. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (Academic Press Inc., New York, 1959).