Rydberg states in polar molecules

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We determine analytically the effect of a point dipole moment on the spectrum and wave functions of Rydberg electron states in polar molecules of arbitrary symmetry. We determine the change required in the Rutherford formula for scattering of a slow electron by an ion of a polar molecule, and calculate the oscillator strength for radiative transitions of a Rydberg electron between discrete levels.

1. INTRODUCTION

Rydberg states of atoms and molecules have been of scientific interest for many years.[1] These states are simpler to describe theoretically than ground states or low-lying excited states—a Rydberg electron in an atom, for example, essentially moves in a pure Coulomb field.

The same opportunity for simplification also exists for Rydberg states in nonpolar molecules. The dipole moment of a polar molecular core, however, significantly alters the motion of a Rydberg electron. In the present paper, we demonstrate that it is possible to allow accurately for the influence of a point dipole moment on a Rydberg electron by appropriately choosing the angular part of the latter's wave function. It then turns out to be possible in general—apart from the case of a dipole of finite dimensions—to classify the Rydberg states of any molecule, including an asymmetric top.

The difficulty of classifying the low-lying states of an asymmetric molecule results from the lack of a symmetry axis for which the projection of the electron angular momentum is conserved. This distinguishes asymmetric molecules from symmetric molecules, which produce Σ,Π,Δ,... terms.[2] For the Rydberg states of a polar molecule, the appropriate symmetry axis lies in the direction of the dipole moment of the molecular core, which is precisely the direction in which the projection of the Rydberg electron's angular momentum is conserved.

In actuality, a Rydberg electron will always be far from the core, and the spherically symmetric Coulomb field will be perturbed mainly by the multipole moments of the core that die off most slowly. Here we have an appealing analogy with the Rydberg states of the noble gases, whose fine structure is attributable to the quadrupole moment of the atomic core.[3] In a polar molecule it is the contribution of the dipole moment that dies off most slowly, and the latter therefore dominates the perturbation of the Coulomb levels. Since the dipole moment is axially symmetric, so are the Rydberg-state wave functions. Thus, if we choose the dipole moment to define the quantization axis in a coordinate system fixed to the molecule, it makes sense to speak of Σ,Π,Δ,... Rydberg states, even when the molecular core as a whole is not axially symmetric.

2. ANGULAR PART OF THE WAVE FUNCTION

Choosing a spherical coordinate system with polar axis in the direction of the dipole moment **d**, we may write the Schrödinger equation for a Rydberg electron in the field of a point dipole:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right)+\frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\Psi}{\partial\varphi^2}\right]+\frac{2\mu}{\hbar^2}\left[E-\frac{ed}{r^2}\cos\theta+\frac{Ze^2}{r}\right]\Psi=0. \qquad (1)$$

Here μ is the mass of the electron and Z is the charge on the molecular core; in general, Z is not necessarily equal to 1.

We now introduce the functions $\tilde{Y}(\beta;\lambda;\theta,\varphi)$, which satisfy the equation

$$-\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\tilde{Y}}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2\tilde{Y}}{\partial\varphi^2}\right]+\beta\cos\tilde{Y}=\lambda\tilde{Y} \qquad (2)$$

and the standard boundary conditions: they are periodic in the azimuthal angle φ with period 2π, and they are regular at $\theta=0$ and $\theta=\pi$.

For $\beta=0$, the $\tilde{Y}$ become the usual spherical harmonics $Y_{lm}(\theta,\varphi)$, with $\lambda=l(l+1)$, $l\geqslant|m|$.

The functions $\tilde{Y}$ make it possible to separate variables in Eq. (1) and write the equation for the radial part of the wave function:

$$\Psi(\mathbf{r})=R(\lambda;r)\tilde{Y}\left(\frac{2\mu ed}{\hbar^2};\lambda;\theta,\varphi\right),$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{\lambda}{r^2}R+\frac{2\mu}{\hbar^2}\left(E+\frac{Ze^2}{r}\right)R=0. \qquad (3)$$

The eigenvalues λ thus define a modified centrifugal energy, which now incorporates the interaction with a point dipole.

The functions $\tilde{Y}$ have been studied in the context of the Stark effect in a linear rotator, both for the weak-field (small β)[4] and strong-field (large β)[5] cases. They have also been utilized to describe bremsstrahlung emitted by an electron scattered by a polar molecule.[6] Reference 6 also cites other papers in which the $\tilde{Y}$ are encountered.

In the present paper, we represent the eigenvalues λ as continued fractions.

For our purposes, it is sufficient to expand the $\tilde{Y}$ in spherical harmonics:

$$\tilde{Y}(\beta;\lambda_m;\theta,\varphi)=\sum_{l=|m|}^{\infty}a_lY_{lm}(\theta,\varphi). \qquad (4)$$

Substituting (4) into (2), we obtain the recurrence relation for the coefficients a_l,

$$\beta\left(\frac{l^2-m^2}{4l^2-1}\right)^{1/2} a_{l-1}+[l(l+1)-\lambda_m]a_l$$

$$+\beta\left[\frac{(l+1)^2-m^2}{(2l+1)(2l+3)}\right]^{1/2} a_{l+1}=0. \tag{5}$$

Nontrivial solutions of the system of equations (5) exist when the determinant of that system vanishes. The vanishing of the determinant then yields the eigenvalues λ.

We list some of the eigenvalues thus obtained in Table I. More detailed data can be found in Refs. 4 (equations) and 5 (plots).

Strictly speaking, the superscript on each eigenvalue λ_m^l denotes its rank in size order. This ordering is a convenient one, however, since the numbers λ_m^l clearly converge quite rapidly to the asymptotic value $l(l+1)$ [as can easily be seen directly from (5)].

Note that states with $m=0$ (Σ terms) have negative eigenvalues λ_m^l, which means that the modified centrifugal energy in Eq. (3) corresponds to an additional attraction of the Rydberg electron toward the moleculear core, beyond that produced by the Coulomb force.

3. PROPERTIES OF THE ANGULAR PART OF THE WAVE FUNCTION

For the sake of brevity, we write

$$\tilde{Y}_{lm}(\beta;\ \mathbf{r})\equiv\tilde{Y}(\beta;\ \lambda_m{}^l;\ \theta,\ \varphi),$$

and where there is no danger of confusion, we omit the variable β.

In this new notation, the expansion (4) becomes

$$\tilde{Y}_{lm}(\beta;\mathbf{r})=\sum_{l'=|m|}^{\infty} a_{ll'}^{m}(\beta)Y_{l'm}(\theta,\varphi). \tag{6}$$

By virtue of the symmetry of the matrix describing the set of linear equations (5), the coefficients $a_{ll'}^m$ can be assumed to be positive. Their values are then uniquely given by

$$\lim_{\beta\to 0} a_{ll'}^{m}(\beta)=\delta_{ll'}. \tag{7}$$

Since the differential operator in (2) is Hermitian, the functions $\tilde{Y}$ are orthogonal, which, together with their completeness, yields

$$\sum_l a_{l_1l}^{m}a_{l_2l}^{m}=\sum_l a_{ll_1}^{m}a_{ll_2}^{m}=\delta_{l_1l_2}. \tag{8}$$

Changing the sign of the dipole moment in the recurrence relation (5) and making use of (7), we have

$$a_{ll'}^{m}(-\beta)=(-1)^{l+l'}a_{ll'}^{m}(\beta). \tag{9}$$

We thus obtain the way in which the $\tilde{Y}$ transform under spatial inversion:

$$\tilde{Y}_{lm}(\beta;\ -\mathbf{r})=(-1)^l\tilde{Y}_{lm}(-\beta;\ \mathbf{r}). \tag{10}$$

4. RADIAL FUNCTIONS FOR BOUND STATES

The solutions of Eq. (3) are formally no different from the solutions of the corresponding Coulomb problem with no dipole potential, and they can thus be expressed in terms of the Whittaker function that is regular at $r=0$. To within a normalization factor,

$$R_\nu(\lambda_m{}^l;r)=\frac{1}{r}M_{\nu,\rho}\left(\frac{(-8\mu E)^{1/2}}{\hbar}r\right),$$

$$\nu=\frac{2\mu Ze^2}{\hbar(-8\mu E)^{1/2}},\quad \rho\equiv\rho_{lm}=(\lambda_m{}^l+{}^1/_4)^{1/2}. \tag{11}$$

The energy quantization conditions follow from the requirement that the functions (11) remain finite as $r\to\infty$, which is true when the Whittaker function reduces to a polynomial:

$$E_{n_r lm}=-\frac{\mu(Ze^2)^2}{2\hbar^2(n_r+\rho+{}^1/_2)^2}=-\frac{Z^2}{\nu^2}\mathrm{Ry},\quad \nu=n_r+\rho+{}^1/_2, \tag{12}$$

where $n_r=0,1,2...$ is the radial quantum number. Naturally, when $\lambda_m^l=l(l+1)$, Eq. (12) yields the familiar energy spectrum of a hydrogen-like atom: $E_n=-\mathrm{Ry}\,Z^2/n^2$, $n=n_r+l+1$. In general, both the effective principal quantum number ν and the spectral energy $E_\nu\equiv E_{n_r lm}$ depend on the values of the quantum numbers l and m.

When $\lambda_m^l<-1/4$, the eigenvalues (12) are no longer real, and the bound states become unstable. This is the well-known case of the Rydberg electron "falling to the center" (Ref. 2, §35). In the present case, the lack of stable bound states implies that the point dipole approximation is inapplicable.

A calculation shows that $\lambda_m^l<-1/4$ first for Σ terms when the dimensionless dipole moment $\beta>1.28$, which cor-

TABLE I. Eigenvalues λ_m^l.

β	$m=0$			$m=1$			$m=2$		
	$l=0$	$l=1$	$l=2$	$l=1$	$l=2$	$l=3$	$l=2$	$l=3$	$l=4$
0,4	−0,026	2,016	6,004	1,992	6,002	12,001	5,996	12,000	20,000
0,8	−0,103	2,060	6,015	1,968	6,007	12,005	5,985	12,000	20,002
1,2	−0,222	2,126	6,035	1,929	6,016	12,012	5,976	12,000	20,005
1,6	−0,376	2,204	6,062	1,874	6,028	12,021	5,939	12,000	20,007
2,0	−0,557	2,287	6,098	1,805	6,042	12,033	5,905	11,999	20,010
2,4	−0,759	2,369	6,143	1,722	6,058	12,048	5,864	11,999	20,014
2,8	−0,978	2,443	6,197	1,627	6,075	12,065	5,816	11,998	20,020
3,2	−1,210	2,509	6,260	1,519	6,092	12,084	5,760	11,997	20,026
3,6	−1,453	2,563	6,332	1,400	6,108	12,107	5,698	11,994	20,033
4,0	−1,704	2,602	6,413	1,270	6,123	12,131	5,629	11,992	20,040

responds to $d > 1.62D$. To describe the Σ terms of molecules which such large dipole moments, it is necessary to somehow regularize the dipole potential at small distances. There are, however, a great many molecules for which the point dipole approximation holds for all terms. These include all of the nitrogen oxides, CO, NH_3, and $CHCl_3$, among others.

To conclude this section, we present the normalized radial eigenfunctions in terms of confluent hypergeometric functions and associated Laguerre polynomials:

$$\begin{aligned} R_{\nu lm}(r) &\equiv R_\nu(\lambda_m{}^l; r) \\ &= \frac{1}{\nu r \Gamma(2\rho+1)} \left[\frac{\Gamma(\nu+\rho+{}^1/_2)}{a n_r!}\right]^{1/2} \left(\frac{2r}{a\nu}\right)^{\rho+1/2} \\ &\times e^{-r/a\nu} {}_1F_1\left(-n_r; 2\rho+1; \frac{2r}{a\nu}\right) = \frac{1}{\nu r}\left[\frac{n_r!}{a\Gamma(\nu+\rho+{}^1/_2)}\right]^{1/2} \\ &\times \left(\frac{2r}{a\nu}\right)^{\rho+1/2} e^{-r/a\nu} L_{n_r}^{2\rho}\left(\frac{2r}{a\nu}\right). \end{aligned} \tag{13}$$

Here $a = \hbar^2/\mu Z e^2$ is the Bohr radius for a hydrogen-like atom with charge Z.

5. CONTINUOUS SPECTRUM

If we assume in Eq. (11) that $E = \hbar^2 k^2/2\mu$, we may write the solution of Eq. (3) for positive energies:

$$R_{klm}(r) = \frac{N_{klm}}{r} M_{-i\varkappa,\rho}(2ikr), \qquad \varkappa \equiv Z/ka. \tag{14}$$

where N is a normalization factor. The asymptotic behavior of (14) is given by

$$\begin{gathered} R_{klm}(r) \sim \frac{2}{r} \sin\left[kr + \varkappa \ln 2kr - \frac{\pi}{2}\left(\rho - \frac{1}{2}\right) + \eta_{lm}\right], \\ \eta_{lm} = \arg\Gamma\left(\rho + \frac{1}{2} - i\varkappa\right), \end{gathered} \tag{15}$$

if N takes the form

$$N_{klm} = \frac{|\Gamma(\rho + {}^1/_2 + i\varkappa)|}{\Gamma(2\rho+1)} \exp\left[\frac{\pi}{2}\varkappa - i\frac{\pi}{2}(\rho + {}^1/_2)\right]. \tag{16}$$

The functions (14) are then normalized on the "wave number scale" (Ref. 2, §33):

$$\int_0^\infty r^2 R_{klm}(r) R_{k'lm}(r)\, dr = 2\pi\delta(k-k'). \tag{17}$$

The quantities η and $\pi(\rho - 1/2)/2$ in (15) embody the influence of the dipole moment on the scattering phase of the electron. In a pure Coulomb field, η becomes the well-known Coulomb phase, and $\pi(\rho - 1/2)/2 \to \pi l/2$.

As in the case of bound states, when $\lambda^l_m < -1/4$, ρ is a complex quantity and the scattering phase is no longer a viable concept. Under those circumstances, scattering from a dipole and scattering from a spherically symmetric $1/r^2$ potential are indistinguishable.[7]

If we formally introduce the principle quantum number $n = n_r + l + 1$, Eq. (12) can be rewritten in the form adopted in the theory of atomic Rydberg states,

$$E_{nlm} = -\frac{Z^2}{(n-\delta_{lm})^2}\,\mathrm{Ry}, \tag{18}$$

where $\delta_{lm} = l + 1/2 - \rho$ is the quantum defect. Comparing this expression with (15), we see that when $k \to 0$, we obtain the usual relationship between the quantum defect and the scattering phase from a pure Coulomb potential,

$$\sigma_{lm} \equiv \frac{\pi}{2}\left(l + \frac{1}{2} - \rho\right) + \arg\frac{\Gamma(\rho + {}^1/_2 - i\varkappa)}{\Gamma(l+1+i\varkappa)}, \tag{19}$$

for $k \to 0$, usually the following relation is valid:[7]

$$\sigma_{lm} = \pi\delta_{lm}. \tag{20}$$

6. SCATTERING AMPLITUDE FOR A SLOW ELECTRON

The above expressions for the wave functions of the continuous spectrum can be employed to derive the cross section for scattering of an electron from an ionized polar molecule. In that event, however, the electron must be moving slowly enough that attention can be restricted solely to scattering by the Coulomb and dipole fields. The formal condition for this approximation to hold is then

$$ka_0 \ll 1, \tag{21}$$

where a_0 is the scale length for the molecular core.

The general theory of scattering in a nonspherical potential has been developed by Demkov and Rudakov[8] (see also Ref. 9). No explicit allowance was made in either Ref. 8 or 9 for the possibility of odd-parity terms in the Hamiltonian, however, so we derive the equations for the amplitudes here.

Let $\mathbf{n}$ and $\mathbf{n}'$ be the direction in which the electron is moving before and after scattering. The scattering amplitude may be derived from the asymptotic behavior of the wave function,

$$\Psi(\mathbf{r}) \sim e^{i\mathbf{kr}} + f(\mathbf{n}, \mathbf{n}')\frac{e^{ikr}}{r}. \tag{22}$$

It should be noted that (22) is in this case heuristic, since it contains only the leading (exponential) terms of the asymptote. Owing to the slow damping of the scattering potential, the asymptote of the wave function acquires also power-law terms[2,9] due in particular to the logarithmic growth of the scattering phases in the Coulomb field. However, the exponential terms already written out make it possible to separate unambiguously from the wave function the incident and scattered waves, while the omitted power-law terms do not change this interpretation.

We can then expand the electron wave function dictated by the asymptotic behavior (22):

$$\Psi(\mathbf{r}) = \sum_{lm} A_{lm}^{(+)} R_{klm}(r) \tilde{Y}_{lm}(\beta; \mathbf{r}). \tag{23}$$

Substituting the asymptotic behavior of the function R_{klm} given by (15), and making use of the asymptotic expansion of a plane wave,

$$e^{i\mathbf{kr}} \sim \frac{4\pi}{kr}\sum_{lm} i^l \sin\left(kr - \frac{\pi l}{2}\right) Y_{lm}^*(\mathbf{k}) Y_{lm}(\mathbf{r}),$$

we can extract the amplitude from Eq. (22):

$$
\begin{aligned}
f(\mathbf{n},\mathbf{n}') &= \lim_{r\to\infty} r\exp\{-ikr\}\,[\Psi(\mathbf{r})-e^{i\mathbf{kr}}] \\
&= -i\lim_{r\to\infty}\exp\{-ikr\}\sum_{lm}\{[(-i)^l A_{lm}^{(+)}(\mathbf{k})\tilde{Y}_{lm}(\beta;\mathbf{r}) \\
&\quad\times\exp\{i(kr-\zeta_{lm})\} \\
&\quad-\frac{2\pi}{k}\tilde{Y}_{lm}^{*}(\mathbf{k})\,Y_{lm}(\mathbf{r})e^{ikr}\Big] \\
&\quad-\Big[i^l A_{lm}^{(+)}(\mathbf{k})\tilde{Y}_{lm}(\beta;\mathbf{r})\exp\{-i(kr+\zeta_{lm})\} \\
&\quad-\frac{2\pi}{k}(-1)^l Y_{lm}^{*}(\mathbf{k})\,Y_{lm}(\mathbf{r})\exp\{-ikr\}\Big]\Big\}, \\
\zeta_{lm} &= \varkappa\ln 2kr-\frac{\pi}{2}\left(\rho-l-\frac{1}{2}\right)+\eta_{lm}, \\
&\mathbf{n}=\mathbf{k}/k,\quad \mathbf{n}'=\mathbf{r}/r.
\end{aligned}
\tag{24}
$$

The limit in (24) exists if the coefficient of the incoming spherical wave vanishes. This condition yields the equation for the coefficients,

$$
\sum_l i^l A_{lm}^{(+)}(\mathbf{k})\tilde{Y}_{lm}(\beta;\mathbf{r})\exp\{-i\zeta_{lm}\}
=\frac{2\pi}{k}\sum_l(-1)^l Y_{lm}^{*}(\mathbf{k})\,Y_{lm}(\mathbf{r}),
$$

which can easily be solved by using Eqs. (8) and (9):

$$
A_{lm}^{(+)}(\mathbf{k})=\frac{2\pi}{k}i^l\exp\{i\zeta_{lm}\}\tilde{Y}_{lm}^{*}(-\beta;\mathbf{k}). \tag{25}
$$

We then have

$$
\begin{aligned}
f(\mathbf{n},\mathbf{n}')=\frac{2\pi}{ik}\sum_{lm}&[\exp\{2i\zeta_{lm}\}\tilde{Y}_{lm}^{*}(-\beta;\mathbf{n})\tilde{Y}_{lm}(\beta;\mathbf{n}') \\
&-Y_{lm}^{*}(\mathbf{n})\,Y_{lm}(\mathbf{n}')].
\end{aligned}
\tag{26}
$$

The last term of Eq. (26) is a delta function by virtue of the completeness of the sperical harmonics. We can thus rewrite the amplitude in the equivalent form

$$
\begin{aligned}
f(\mathbf{n},\mathbf{n}')=\frac{2\pi}{ik}\sum_{lm}&[\exp\{2i\zeta_{lm}\}\tilde{Y}_{lm}^{*}(-\beta;\mathbf{n}) \\
&-\tilde{Y}_{lm}^{*}(\beta;\mathbf{n})]\tilde{Y}_{lm}(\beta;\mathbf{n}').
\end{aligned}
\tag{27}
$$

In the limit of spherical symmetry ($\beta\to 0$), Eqs. (26) and (27) yield the usual expression for the scattering amplitude in a central field.

Using Eq. (10) and the fact that the phase ζ_{lm} are independent of the sign of m, it can be shown that the amplitude satisfies a reciprocity relation, indicating that the scattering process is T-invariant:[2]

$$
f(\mathbf{n},\mathbf{n}')=f(-\mathbf{n}',-\mathbf{n}).
$$

The unitarity of the amplitude is also directly demonstrable.

To conclude this section, we write out an expression analogous to (25) for the coefficients $A_{lm}^{(-)}$, which in accordance with (23) determine the continuous-spectrum wave function corresponding to "plane wave + incoming spherical wave" asymptotic behavior:

$$
A_{lm}^{(-)}(\mathbf{k})=\frac{2\pi}{k}i^l\exp\{-i\zeta_{lm}\}\tilde{Y}_{lm}^{*}(\beta;\mathbf{k}). \tag{28}
$$

7. SCATTERING CROSS SECTION

The equations for the scattering amplitude derived in the preceding section enable us to calculate the differential cross section, and in particular, to find the corrections to the Rutherford formula for a slow electron scattered by a molecular ion.

If we disregard forward scattering, for which of course the Rutherford cross section diverges, we can drop terms from Eqs. (26) and (27) that do not contain the phase ζ_{lm}. Having done so, we can then omit the divergent term ln $2kr$, which is a factor common to all of the partial amplitudes. Furthermore, the calculations are facilitated by explicitly extracting from the amplitude that part due exclusively to the Coulomb field. The net result for the differential cross section is then

$$
\begin{aligned}
\frac{d\sigma}{d\mathbf{n}'}=\Big|\frac{2\pi}{ik}\sum_{lm}&\exp\{2i\eta_l{}^c\}[\exp\{2i\sigma_{lm}\}\tilde{Y}_{lm}^{*}(-\beta;\mathbf{n})\tilde{Y}_{lm}(\beta;\mathbf{n}') \\
&-Y_{lm}^{*}(\mathbf{n})\,Y_{lm}(\mathbf{n}')]-f_C(\Theta)\Big|^2,
\end{aligned}
\tag{29}
$$

$$
f_C(\Theta)=-\frac{\varkappa}{2k\sin(\Theta/2)}\frac{\Gamma(1-i\varkappa)}{\Gamma(1+i\varkappa)}\exp\left(2i\varkappa\ln\sin\frac{\Theta}{2}\right),
$$

where $\eta_l^C=\arg\Gamma(l+1-i\varkappa)$ is the finite part of the Coulomb phase, σ_{lm} is given by (19), f_C is the Coulomb amplitude, and $\Theta=\cos^{-1}(\mathbf{nn}')$ is the scattering angle.

In practice, the quantity of most interest is the cross section (29) averaged over orientations of the dipole moment. To carry out the averaging, we transform to a coordinate system in which the z axis is directed along $\mathbf{n}$. In that system, the polar angle of the dipole moment is obviously θ, and the azimuthal angle is effectively arbitrary. As before, we denote the latter by φ.

Recalling, then, that

$$
\lim_{\theta\to 0}Y_{lm}(\theta,\varphi)=\left(\frac{2l+1}{4\pi}\right)^{1/2}\delta_{m0},
$$

we have

$$
\begin{aligned}
\frac{d\sigma}{d\mathbf{n}'}=\Big|(4\pi)^{1/2}&\sum_{ll'l''mm'}(2l''+1)^{1/2}B_{ll'l''}^{(l'')*} \\
&\times D_{0m}^{(l'')*}(\varphi,\theta,0)D_{m'm}^{(l')}(\varphi,\theta,0)\,Y_{l'm}(\mathbf{n}')-f_C(\Theta)\Big|^2,
\end{aligned}
$$

$$
\begin{aligned}
B_{ll'l''}^{m}=\frac{1}{2ik}&\exp\{2i\eta_l{}^c\}[\exp\{2i\sigma_{lm}\}a_{l''}^{m}(-\beta)a_{ll'}^{m}(\beta) \\
&-\delta_{ll'}\delta_{ll''}].
\end{aligned}
$$

The D matrices here represent finite rotations. Making use of the usual relations from angular momentum thoery, we can average over θ and φ in the expression that we have derived, yielding

$$\left\langle\frac{d\sigma}{d\mathbf{n}'}\right\rangle=|f_C(\Theta)|^2-2\,\mathrm{Re}\left[f_C^*(\Theta)\sum_{ll'm}B^{m}_{ll'l'}P_{l'}(\cos\Theta)\right]$$

$$+\sum_{\substack{ll'l''mL\\ jj'j''m'J}}{}' (-1)^{l'+j'+J+m+m'}[(2l'+1)(2l''+1)$$

$$\times(2j'+1)(2j''+1)]^{1/2}$$

$$\times B^{m}_{ll'l''}B^{m'*}_{jj'j''}C^{L0}_{l'0j'0}C^{L0}_{l''0j''0}C^{J0}_{j'm'j''-m'}W(l''l'j''j';JL)P_L(\cos\Theta), \tag{30}$$

where the P are Legendre polynomials. The first term in Eq. (30) is the Rutherford term, and the last is the pure dipole contribution to the cross section. The second term is due to interference between the Coulomb and dipole potentials.

Equation (30) is difficult to analyze. We therefore make use of (21) to simplify it, since the error committed is minor if we take $a\approx a_0$. Representing the phases η_l^C and σ_{lm} up through the leading terms in $\varkappa$, we obtain

$$k^2\left\langle\frac{d\sigma}{d\mathbf{n}'}\right\rangle=\frac{\varkappa^2}{4\sin^4(\Theta/2)}-\frac{\varkappa}{2\sin^2(\Theta/2)}$$

$$\times\sum_{ll'm}\left\{(-1)^{l+l'}\sin\left[2\varkappa\ln\sin\frac{\Theta}{2}\right.\right.$$

$$\left.-2\pi\left(l+\frac{1}{2}-\rho_{lm}\right)\right][a^{m}_{ll'}(\beta)]^2$$

$$\left.-\sin\left(2\varkappa\ln\sin\frac{\Theta}{2}\right)\delta_{ll'}\right\}P_{l'}(\cos\Theta)$$

$$+\frac{1}{4}\sum_{\substack{ll'l''mL\\ jj'j''m'J}}(-1)^{l'+j'+J+m+m'}[(2l'+1)(2l''+1)$$

$$\times\ (2j'+1)(2j''+1)]^{1/2} \tag{31}$$

$$\times C^{L0}_{l'0j'0}C^{L0}_{l''0j''0}C^{J0}_{j'm'j''-m'}W(l''l'j''j';JL)$$

$$\times\ \left[\exp\left\{2\pi i\left(l+\frac{1}{2}-\rho_{lm}\right)\right\}\right.$$

$$\left.\times a^{m}_{ll'}(-\beta)a^{m}_{ll''}(\beta)-\delta_{ll'}\delta_{ll''}\right]\left[\exp\left\{-2\pi i\left(j+\frac{1}{2}-\rho_{jm}\right)\right\}\right.$$

$$\left.\times a^{m}_{jj'}(-\beta)a^{m}_{jj''}(\beta)-\delta_{jj'}\delta_{jj''}\right].$$

Clearly, when (21) holds, the main corrections to the Rutherford scattering formula are due to the interference term in the cross section. By way of illustration, we present some numerical values of these corrections for $\beta=1$. One convenient parametrization of the cross section is then

$$k^2\left\langle\frac{d\sigma}{d\mathbf{n}'}\right\rangle\approx\frac{\varkappa^2}{4\sin^4(\Theta/2)}-\frac{\varkappa}{2\sin^2(\Theta/2)}$$

$$\times\sum_{i=0}b_i\sin\left(2\varkappa\ln\sin\frac{\Theta}{2}+\gamma_i\right)P_i(\cos\Theta).$$

We list the coefficients b_i and phases γ_i:

i:	0	1	2
b_i:	−1,166	0,123	−0,048
γ_i:	0,865	−1,04	−0,57

We see that the sum of Legendre polynomials converges rapidly. At the same time, the corrections are fairly sizable.

8. RADIATIVE TRANSITIONS IN THE DISCRETE SPECTRUM

Electromagnetic transition probabilities are important characteristics of Rydberg states, and a great deal of effort has been devoted to the calculation of oscillator strengths for Rydberg-state atoms (see, e.g., Refs. 10–13). In this section, we discuss some of the analogous characteristics for the Rydberg states of polar molecules.

In the one-electron nonrelativistic approximation, it is well known that the probability of a dipole transition depends on the matrix element of the electron radius vector,

$$\langle\nu lm|r_\gamma|\nu'l'm'\rangle,\quad \gamma=0,\ \pm1.$$

Here the integration over angular variables is straightforward:

$$\langle\nu lm|r_\gamma|\nu'l'm'\rangle=Q^{ll'}_{m\gamma m'}\int_0^\infty R_{\nu lm}(r)R_{\nu'l'm'}(r)r^3\,dr,$$

$$Q^{ll'}_{m\gamma m'}=\sum_{LL'}\left(\frac{2L'+1}{2L+1}\right)^{1/2}C^{L0}_{L'010}C^{Lm}_{L'm'1\gamma}a^{m}_{lL}(\beta)a^{m'}_{l'L'}(\beta). \tag{32}$$

The radial wave functions in the foregoing integral are given by (13).

One special property of the Rydberg states is that in addition to being hydrogenlike, they are also quasiclassical.[10,11] The fact that the atomic wave functions are also quasiclassical is exactly why the atomic integrals analogous to (32) can be calculated.

The claim that the Rydberg states of polar molecules have quasiclassical wave functions is not always true, the point being that the centrifugal potential λ/r^3 in (3) only satisfies the requirements for applicability of the quasiclassical approximation when $|\lambda|\gg 1$.[2,14] If $\lambda>0$, we can formally circumvent the problem that arises for small λ by making the substitution $\lambda\to\lambda+1/4$, which is analogous to the well-known substitution $l(l+1)\to(i+1/2)^2$ for motion in a centrally symmetric field.

No such substitution exists, however, for $\lambda<0$. Mathematically, the reason is that for $\lambda>0$ the quasiclassical radial integrals that define the wave functions are evaluated between the turning points of the classically allowed motion, while for $\lambda<0$ one of the turning points is replaced by $r=0$, and the integrals diverge. Therefore, in the most interesting case—$\lambda<0$—the integral in (32) cannot be calculated to the same accuracy as the analogous atomic integral.

Nevertheless, the integral in (32) can indeed be calculated to zeroth order in λ/ν, which is entirely adequate for most applications of the theory of Rydberg states. To do so, note that just as for the atomic states, the principal contribution to the integral comes from large r, where the centrifugal potential is much smaller than the Coulomb potential. One can then neglect the λ/r^2 potential in calculating the radial dependence of the wave functions, including it solely in the quantum defects, in the same way that this is done in atomic calculations using the quantum defect method.[15] Assuming that

$$|\nu-\nu'|\ll\nu. \tag{33}$$

we can make use of results derived by Davydkin and Zon.[11] To zeroth order in λ/ν,

$$\langle \nu lm|r_\gamma|\nu' l' m'\rangle \approx Q^{ll'}_{m\gamma m'} \frac{\bar{\nu}^2}{Z\Delta}\frac{d}{dx}\mathbf{J}_\Delta(-x)\,|_{x=\Delta}, \tag{34}$$

where $\Delta = \nu - \nu'$ and **J** is Anger's function $\bar{\nu} = (\nu\nu')^{1/2}$.

In this approximation, the radial integral is clearly independent of l and l', which is not at all surprising. The dependence on l and l' resides wholly within the Q factors, which at the same time distinguish the molecular from the atomic oscillator strengths.

Note that Eq. (34) is even applicable when the noninteger difference between the principal quantum numbers ν and ν' is due not only to dipole moment of the core (12), but to other short-range forces as well. In that sense, the analogy with the atomic quantum defect method is complete.

The calculation required to obtain the radial matrix elements when (33) does not hold are much more involved. Besides determining the radiative transition probabilities between discrete Rydberg states, these matrix elements also determine the probability of photoionization from a Rydberg state.[12] Appropriate results will be published separately.

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