PHYSICAL REVIEW VOLUME 162, NUMBER 1 5 OCTOBER 1967

Pressure Shifts of Highly Excited States of Atoms*

M. H. MITTLEMAN
Space Sciences Laboratory, University of California, Berkeley, California

(Received 3 March 1967)

A reinvestigation is given of Fermi's work on the shift of highly excited states of atoms embedded in a gaseous medium due to the interaction of the active electron with the medium particles. For the case treated by Fermi, spherically symmetric medium particles, it is found that effects neglected by him cancel and that his results are essentially correct. The method is extended to the case where the medium is composed of diatomic molecules, and it is shown that when rotational excitation is not important, only low-energy elastic scattering contributes in a manner similar to the spherically symmetric scatterer. A simple two-rotational-state model is also analyzed in the case where rotational excitation may be important. It is concluded from the model that when the method used is applicable, real rotational coupling is never important.

I. INTRODUCTION

In 1934, Fermi[1] analyzed the shift of highly excited atomic states due to the interaction of the atom with a surrounding atomic medium. He showed that part of the shift could be related to the interaction between the electron and the medium particles (M.P.), and since the electron has essentially zero energy, this was given in terms of the electron-M.P. scattering length. Spectroscopic techniques have now advanced to the point where one can accurately observe the shifts of these levels and thereby measure the scattering length.[2] Shifts of spectral lines of the order of 0.1 cm^{-1} are measurable. Using equations derived below, this implies densities of the order of 10^{16}–10^{17} cm^{-3}, which means an interparticle separation R_1 of the order of 10^{-6} cm. That is, the atoms are separated by the order of 100 times their radius. This will be a useful fact in developing our theory.

This, however, does not appear to be an attractively competing method for making these measurements. The reason is that well-defined electron beams with energies of the order of an electron volt are readily available and the electron-atom cross sections are expected to be reasonably smooth at and below this energy, so that the measurements can easily be extrapolated down to zero energy.[3] Thus, although the "beam" of bound-state electrons of energy Ry/n^2 (we contemplate states of principle quantum number n, of the order 20 to 30) has a very low energy, it is not necessary for this measurement. On the other hand, there are cross sections such as the rotational excitation cross sections of diatomic molecules which are energy-dependent even at such low energies. The separation of the rotational levels of molecules is of the same order as, or smaller than, the separation of the atomic levels in question. Thus the presence of the molecular M.P. might be expected to strongly perturb the observed levels of the atom. The method may then be useful for getting information in energy regions where beams are not readily available.

In Sec. II, the case where the M.P. is a spherically symmetric atom is discussed. This is the problem discussed by Fermi.[1] We have generalized his method to treat nonzero energy electrons, thereby allowing for an energy-dependent cross section, and we make explicit allowance for the long-range nature of the potential interaction between the electron and the M.P. Effects which Fermi did not consider are found to cancel, and the only additional terms are due to the modification of the effective-range formula because of the presence of the long-range potential.

In Sec. II the method is further generalized to allow the M.P. to have different states of excitation which can be coupled by interaction with the electron. The method is then applied to the case in which the medium is made up of nonpolar molecules. In the approximation treated here, the coupling of the rotational states does not play an important role and a result similar to the atomic medium problem is obtained. A treatment in which rotational coupling is treated more carefully would appear to be desirable. Therefore, a model of M.P. with only two rotational states is briefly examined, and it is concluded that real rotational coupling is probably never important.

The basic mathematical method is an averaging procedure due to Fermi. For denser media, this would not be adequate and one would have to resort to multiple-scattering techniques such as those of Watson.[4] However, there is a restriction as to how dense the medium can be, as pointed out in Sec. II, so that the simple method used here is probably all that is necessary in the problem.

II. ATOMIC MEDIA

The experiment contemplated here is that of observing the absorption spectrum of any atomic species (Cs for instance) tenuously distributed in any atomic background gas (Ne for instance). We are interested in excited states of Cs with principle quantum number

---

* Supported by National Aeronautics and Space Administration Grant No. NsG 243.

[1] E. Fermi, Nuovo Cimento **11**, 159 (1934).

[2] Sumner Davis (private communication).

[3] T. F. O'Malley, Phys. Rev. **130**, 1020 (1963).

[4] M. L. Goldberger and K. M. Watson, *Collision Theory* (John Wiley & Sons, Inc., New York, 1965).

$n \simeq 20$ to 30. The requirement that these be well-defined bound states limits the density of the medium since it is necessary that the length of one orbit, $2\pi a_0 n^2$, be much less than a mean free path of an electron in the gas $(\rho\sigma)^{-1}$, or $\rho \ll 5\times10^{20}$ cm^{-3}.

At reasonable temperatures, the velocity of the electron in its orbit is much greater than that of the M.P., so that these may be considered fixed in position. Thus we must consider the Hamiltonian composed of a group of M.P. fixed in position and interacting with a single Cs atom. We can isolate the part of the total wave function which has the medium in its ground state and assume that the rest of the wave function is not strongly coupled.[5] This would seem to be a reasonable approximation here since the characteristic excitation energy of M.P. is a few volts, much greater than the energy of the electron in question. We can thus obtain a Schrödinger equation for the Cs atom alone. It will contain the interaction of the M.P. with the electron and with the Cs core. There will be terms in which the neon atoms are polarized by the core and interact with the electron so that the interaction is not the usual "two-body" one. We neglect this polarization during interaction as a higher-order term. The Schrödinger equation[6] for the electron then becomes

$$\{E-\Delta E-U(r)+\nabla^2\}\psi(r)=\sum_\alpha v(r-Z_\alpha)\psi(r)\,, \tag{1}$$

where Z_α is the position of the αth M.P. and v is the interaction between the electron and the M.P. The sum runs over all M.P. $U(r)$ is the interaction of the electron with the Cs core which for highly excited states may be well approximated by

$$U(r)=-2/r\,. \tag{2}$$

The term ΔE is meant to be the interaction energy of the M.P. with the Cs core. It is sufficient to use the asymptotic form of the polarization potential for the interaction so that

$$\Delta E=-\sum_\beta \alpha/Z_\beta{}^4\,, \tag{3}$$

where α is the polarizability of the M.P. The sum may be converted to an integral over the positions of the M.P. by using $\sum_\beta \to \rho\int d^3Z$, where we have assumed that the density is uniform.[7] Fermi uses the interparticle separation R_1 as a lower limit to the integral, obtaining

$$\Delta E=-3\alpha(\tfrac{4}{3}\pi\rho)^{4/3}\,. \tag{4}$$

Now consider Eq. (1) in the vicinity of one of the scatterers, the βth say. Then is the βth term is excluded from the electron-M.P. potentials on the right side of (1) the remaining terms are a constant differing negligibly from (3), the polarization energy of the M.P. Thus (1) can be rewritten (near $r=Z_\beta$)

$$(p^2(r)+\nabla^2)\psi(r)=v(r-Z_\beta)\psi(r)\,, \tag{5}$$

where the local (constant) momentum $p(r)$ is defined by

$$p(r)^2=E-2\Delta E-U(r)\,. \tag{6}$$

Equation (5) is precisely the equation describing the scattering of an electron of energy $p(r)^2$ by a M.P. The boundary condition dictated for this local problem is at $|r-Z_\beta|=R$ (R is the limit of influence of the single M.P.). $\psi(r)=C\langle\psi(r)\rangle$, where $\langle\psi\rangle$ is the average of ψ over a volume V which is large enough to contain many M.P. but small enough to treat $p(r)$ as a constant. Thus $\langle\psi\rangle$ is the slowly varying part of ψ after the variation due to the individual scatterings is averaged out. C is a constant which will be chosen to be unity (see below). $\langle\psi\rangle$ is constant in the vicinity of $r=Z_\beta$, so that only the s-wave part of the scattering solution contributes. Thus the solution of (5) may be written

$$\psi(r)=\frac{R}{r}\frac{u(r)}{u(R)}\langle\psi(r)\rangle C\,, \tag{7}$$

where $u(r)$ is the regular s-wave radial solution of (5). Now returning to (1) with r out of the region of all scatterers, we may evaluate the right side by using (7). We note that when r is not near any single M.P., the contribution of the sum in (1) must be a constant. Its evaluation is facilitated by averaging the constant over the volume V. In that case the right side of (1) becomes

$$\begin{aligned}\frac{1}{V}\int d^3r\sum_\alpha v(r-Z_\alpha)\psi(r) &=\frac{1}{V}\sum_\alpha\int_\alpha d\tau\, v_\alpha\psi+\frac{1}{V}\sum_\alpha\int_{\delta V} d^3r\, v_\alpha\psi\\ &=\frac{1}{V}\sum_\alpha\int_\alpha d\tau(p^2+\nabla^2)\psi(r)+\frac{1}{V}\sum_\alpha\int_{\delta V} d^3r\, v_\alpha\psi\,.\end{aligned} \tag{8}$$

Here the subscript α indicates that the integral is to be taken inside the "volume of influence" surrounding Z_α, and the subscript δV means that the integral is outside these volumes. The last step is just the use of (5). We have $\delta V=V-\frac{4}{3}\pi R^3N$, so that $\delta V/V=1-\frac{4}{3}\pi R^3\rho$. Thus the total wave function is given by $C\langle\psi\rangle$ outside of the volume of influence of the individual M.P. and by (7) near each M.P. The volume average $\langle\psi\rangle$ then defines the constant C.

$$\langle\psi\rangle=\frac{\delta V}{V}C\langle\psi\rangle+\frac{N}{V}C\langle\psi\rangle\frac{R}{u(R)}\int^R\frac{d^3r}{r}u(r)\,,$$

which may be solved for C to give

$$C=\left[1-\tfrac{4}{3}\pi R^3\rho\left(1-\frac{3}{R^2u(r)}\int_0^R rdr\, u(r)\right)\right]^{-1}. \tag{8a}$$

---

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

[6] Rydberg units are used here and below.

[7] The correction due to the correlation of the M.P. with the Cs core is negligible at room temperature.

In general, C differs only slightly from unity. Our subsequent calculations will be greatly simplified by choosing R to be one of the solutions of

$$\tfrac{1}{3}R^2u(R)=\int_0^R rdr\,u(r)\,, \qquad (8b)$$

giving $C=1$. This can be done since $u(R)$ is an oscillating function. We shall see that our results do not depend critically upon this choice. Now the Laplacian in (8) may be converted to a surface integral yielding

$$\frac{1}{V}\int d^3r\sum_{\alpha} v_\alpha\psi=\tfrac{4}{3}\pi R^3\rho p^2\langle\psi\rangle$$
$$+4\pi R^2\rho\frac{\partial}{\partial r}\left(\frac{R}{r}\frac{u(r)}{u(R)}\right)_{r=R}\langle\psi\rangle-\frac{4\pi\alpha\rho}{R}\langle\psi\rangle\,, \qquad (9)$$

where we have used (8b) and the relation $(1/V)\sum_\alpha=\rho$. The last term results from the last term in (8). It is evaluated by using the long-range form of v_α. The integrals and sums are performed as described in connection with Eq. (3). Thus the averaged Eq. (1) becomes

$$(E-\Delta E-U(r)+\nabla^2)\langle\psi\rangle$$
$$=\tfrac{4}{3}\pi R^3\rho\left(p^2+\frac{3}{R}\frac{\partial}{\partial r}\left(\frac{R}{r}\frac{u(r)}{u(R)}\right)_{r=R}-\frac{3\alpha}{R^4}\right)\langle\psi\rangle. \qquad (10)$$

R is large enough so that $u(r)$ may be evaluated in terms of its asymptotic form and the right side of (10) may be expressed in terms of the s-wave phase shift for electron M.P. scattering. If v is a short-range potential, this simply means that R must be greater than the range. For long-range potentials, the considerations are a bit more complicated. We consider short-range potentials first.

In that case, R may be assumed to be larger than the range and the right side of (10) becomes

$$\tfrac{4}{3}\pi R^3\rho\left(p^2+(3/R)[-1/R+p\cot(pR+\delta)]-3\alpha/R^4\right)\langle\psi\rangle,$$

where δ is the p^2-dependent s-wave phase shift. This should be treated as a potential term in (10), the r dependence entering through $p(r)$ and $\delta(p)$. However, we note that p will be very small, so that an expansion in pR is possible. Then this becomes

$$-4\pi\rho\left[\frac{(\tan\delta)/p}{1+(\tan\delta)/pR}+\frac{\alpha}{R}\right]\langle\psi\rangle.$$

If we further assume that $R\gg(\tan\delta)/p$, which is the case considered by Fermi, then Eq. (10) may be written

$$[E-\Delta E-U(r)+\nabla^2]\langle\psi\rangle$$
$$=-4\pi\rho[(\tan\delta)/p+\alpha/R]\langle\psi\rangle\,, \qquad (11)$$

and if an effective range expansion[4] is made for $\tan\delta$, this becomes

$$(\mathcal{E}-Z_eU+\nabla^2)\langle\psi\rangle=0\,, \qquad (12)$$

where

$$\mathcal{E}=Z_e(E-\Delta E)-4\pi\rho A+4\pi\rho\alpha/R \qquad (13a)$$

and

$$Z_e=1-2\pi\rho A^2r_0. \qquad (13b)$$

Here A is the scattering length and r_0 is the effective range. Equation (12) is easily solved. The eigenvalues are $\mathcal{E}_n=-Z_e^2/n^2$. The unshifted eigenvalues are $E_n^{(0)}=-1/n^2$, so that the shift of the level is given by

$$\Delta E_n=E_n-E_n^{(0)}\simeq 2\pi\rho A^2r_0/n^2+\Delta E+4\pi A\rho$$
$$-4\pi\rho\alpha/R, \qquad (14)$$

where only lowest order in the density has been retained. The state-dependent term is new, but very small at densities of interest unless the scattering length and effective range are very large.

The method used here is somewhat inconsistent. The long-range potential is used to evaluate ΔE but is ignored in the scattering functions u, entering in Eq. (10). Therefore, we now turn to considerations of long-range potentials in the scattering. We limit these to polarization potentials

$$v(r)\sim-\alpha/r^4. \qquad (15)$$

There are two changes in the result (14) due to the long-range potential. The first is the modification of the effective-range formula[8] and the second is the modification of $u(r)$ in (10) (see Appendix A). These yield an additional term on the right side of (11) of the form

$$\langle\psi\rangle4\pi\alpha\rho[\tfrac{1}{3}\pi p+\tfrac{4}{3}Ap^2\ln(\tfrac{1}{4}p\alpha^{1/2})+1/R]\,, \qquad (16)$$

which yields an equation of motion replacing (12).

$$[E-\Delta E-u(r)+\nabla^2]\langle\psi\rangle=4\pi\rho[A+\tfrac{1}{3}\alpha\pi p(r)$$
$$+\tfrac{4}{3}\alpha Ap^2(r)\ln(\tfrac{1}{4}p(r)\alpha^{1/2})]\langle\psi\rangle. \qquad (17)$$

Notice that the R dependence has been cancelled by the consistent treatment of the long-range potential. The r dependence on the right side of (17) can be treated as a perturbation because of the smallness of ρ. The resultant shift in the energy level is[9]

$$\Delta E_{nl}=\Delta E+4\pi\rho A$$
$$+\tfrac{4}{3}\pi\rho\alpha[\pi p_{nl}+4A(p^2\ln(\tfrac{1}{4}p\alpha^{1/2}))_{nl}]\,, \qquad (18)$$

where the subscript (n,l) indicates an expection with respect to the hydrogenic state (n,l). Note that $p(r)$ becomes imaginary for sufficiently large values of $r(r\sim n^2)$. It may be set equal to zero for these values of r without any signficant error. Fermi's result is just the first two terms of (18). A consistent treatment of the "excluded volume" effects and the distortion of the wave function cancel and the simple results are restored.

---

[8] L. Spruch, T. F. O'Malley, and L. Rosenberg, Phys. Rev. Letters 5, 375 (1960).

[9] The existence of this state-dependent shift has previously been noted by J. Ehrhardt.

The expansions leading to (17) are not completely necessary. If the interparticle spacing R_1 is large enough so that $u(R)$ may be evaluated where the potential v is simple (i.e., $\sim r^{-4}$), then the right side of Eq. (10) may be expressed in terms of the known radial functions in these potentials and the residual phase shifts.[8]

III. MOLECULAR MEDIA

We now turn to the more complex problem of a medium composed of diatomic molecules. In this case no single state of the medium decouples from the rest. Thus we must consider a wave function which is a superposition of many medium states. As before, the M.P. are fixed in positions Z_α with wave functions $g(\nu_\alpha)$ and energy eigenvalues $w(\nu_\alpha)$. The molecules will all be assumed to be in their ground-electronic state in a distribution of vibrational states. But as before, the coupling between the vibrational states due to the interaction with the electron will be neglected. However, the coupling between the rotational levels will not be negligible. We designate the state of the medium by the notation

$$|s\rangle = |\nu(s_1)\nu(s_2)\cdots\nu(s_N)\rangle,$$

indicating that the αth particle is in the state $\nu(s_\alpha)$. The total wave function is projected onto the subspace

$$P\psi=\sum_s \phi_s(r)|s\rangle, \tag{19}$$

where the sum covers all the rotational states of the molecules.

As in Sec. II, we neglect the interaction of the electron with polarized M.P. The Schrödinger equation for the ϕ_s is

$$[E_s-U(r)+\nabla^2]\phi_s(r)=\sum_\alpha\sum_{s'} v_{ss'}(r-Z_\alpha)\phi_{s'}(r), \tag{20}$$

where $v_{ss'}$ is the coupling potential between the states s and s' of the M.P. Note that only medium states differing only by the state of the αth particle can be coupled by $v_{ss'}(r-Z_\alpha)$. The channel energies E_s are given by

$$E_s=E-\mathcal{E}_s-\Delta\mathcal{E}_s, \tag{21}$$

where $\mathcal{E}_s$ is the energy of the isolated medium in state s

$$\mathcal{E}_s=\sum_{s=1}^{N} w(\nu_s) \tag{22}$$

and $\Delta\mathcal{E}_s$ is the interaction of the Cs core with the medium. Strictly speaking, this interaction couples different states of the M.P., but we neglect these off-diagonal terms as small. Then $\Delta\mathcal{E}_s$ may be evaluated as in Sec. II. The only difference is that we must allow for the different polarizabilities parallel and perpendicular to the internuclear line. The result is

$$\Delta\mathcal{E}_s=\Delta\mathcal{E}=-(\alpha_{\parallel}+2\alpha_{\perp})(\tfrac{4}{3}\pi\rho)^{4/3}=-3\alpha(\tfrac{4}{3}\pi\rho)^{4/3}, \tag{23}$$

which is independent of s in the Born-Oppenheimer approximation for the molecules.

In the vicinity of the βth M.P., Eq. (20) becomes

$$(p_s^2+\nabla^2)\phi_s(r)=\sum_{s'} v_{ss'}(r-Z_\beta)\phi_{s'}(r), \tag{24}$$

where, as before,

$$p_s^2(r)=E-2\Delta\mathcal{E}-\mathcal{E}_s-U(r). \tag{25}$$

Now the index s will vary only over medium states in which all but the βth M.P. have fixed states, but the βth is changed due to the electron collision. These equations describe the scattering of an electron from a molecule. It is advantageous to obtain the solution in a representation in which total angular momentum is conserved. To this end we write

$$\phi^{LM}(rl_0l_0')=\sum_{lml'm'}\frac{1}{r}u_{ll_0}(r,l'l_0')g_{l'}|lml'm'\rangle \times\langle lml'm'|LMll'\rangle. \tag{26}$$

Here $g_{l'}Y_{l'm'}\equiv g_{l'}|l'm'\rangle$ is the rotational wave function of the βth M.P. and the last factor is the usual vector coupling coefficient. The index ν_β used above is now explicitly written as $l'm'$. The dependence on the rest of the M.P. has been suppressed since it enters only parametrically into the equations for the radial wave functions u which are

$$\left[p_{l'}^2+\frac{d^2}{dr^2}-\frac{l(l+1)}{r^2}\right]u_{ll_0}(r,l'l_0') =\sum_{mm'\lambda\lambda'\mu\mu'}\langle LMll'|lml'm'\rangle\langle lml'm'|g_{l'}vg_{\lambda'}|\lambda\mu\lambda'\mu'\rangle \times\langle\lambda\mu\lambda'\mu'|LM\lambda\lambda'\rangle u_{\lambda l_0}(r,\lambda'l_0'). \tag{27}$$

The dependence of u upon L has also been suppressed. The boundary conditions are taken to be

$$u_{ll_0}(r,l'l_0')\underset{r\to\infty}{=}\frac{\sin(p_{l'}r-l\pi/2)}{p_{l'}}\delta_{ll_0}\delta_{l'l_0'} +\frac{K_{ll',l_0l_0'}}{(p_{l'}p_{l_0'})^{1/2}}\cos(p_{l'}r-l\pi/2), \tag{28}$$

where

$$p_{l'}^2(r)=E-2\Delta\mathcal{E}-\sum_{s=1;\,s\neq\beta}^{N} w(l_s)-w(l')-U(r). \tag{29}$$

Here K, the coefficient of the scattered wave, is simply related to the usual reaction matrix for the transition of the molecule in state l_0' and the electron in relative partial wave l_0 to the state l' and l, respectively. We must now solve the boundary-value problem and, as in Sec. II, obtain a superposition of solutions (26) to give the function $\langle\phi_s\rangle$ at $r=R$. That is, we require that a general solution

$$\psi_\beta(r)=\sum_{s_\beta}\sum_{LMl_0l_0'}A^{LM}(l_0,l_0')\phi^{LM}(r,l_0l_0')|s_\beta\rangle \tag{30}$$

satisfy the boundary condition

$$\psi_\beta(r)|_{r=R}=\sum_s|s\rangle\langle\phi_s\rangle. \tag{31}$$

In (30) the notation $|s_\beta\rangle$ means the medium states with the βth wave function omitted. It is included in ϕ^{LM} and labeled by $l'm'$. Substitution of (26) and (30) into (31) and some obvious use of orthogonality properties of the wave functions yields

$$\sum_{l_0l_0'}u_{ll_0}(R,l'l_0')A^{LM}(l_0l_0')=(4\pi)^{1/2}R\delta_{l0}\delta_{Ll'}\langle\phi_s\rangle. \tag{32}$$

A slight simplification results from the substitution

$$A^{LM}(l_0l_0')=(4\pi)^{1/2}R\langle\phi_s\rangle\Gamma(L,l_0l_0'), \tag{33}$$

so that (32) becomes

$$\sum_{l_0l_0'}u_{ll_0}(R,l'l_0')\Gamma(L,l_0l_0')=\delta_{l0}\delta_{Ll'}. \tag{34}$$

If Γ is known, the solution in the vicinity of the βth M.P. can be constructed:

$$\psi_\alpha(r)=\sum_{sl_0l_0'}s\rangle\langle\phi_s\rangle\frac{R}{r}u_{0l_0}(r,l'l_0')\Gamma(l',l_0l_0'), \tag{35}$$

where we have now taken explicit note of the fact that only the spherically symmetric part of ψ will survive. Now returning to our starting point, Eq. (20), we again consider the equation far from any M.P. and resort to the averaging procedure leading to Eq. (10). The result is

$$[E_s-U(r)+\nabla^2]\langle\phi_s(r)\rangle=\frac{1}{V}\sum_\alpha\biggl(p_s^2\langle\phi_s\rangle$$
$$+\frac{3}{R}\frac{\partial}{\partial r}\langle s|\psi_\alpha(r)\rangle\biggr|_{r=R}-\frac{3\alpha}{R^4}\langle\phi_s\rangle\biggr)\tfrac{4}{3}\pi R^3. \tag{36}$$

In order to evaluate the last term, a solution of (34) for Γ is necessary. We accomplish this by noting that for low energy the electron-molecule elastic cross sections are much greater than the inelastic ones.[10] We therefore break the u's into diagonal and off-diagonal parts;

$$u_{ll_0}(r,l'l_0')=\delta_{ll_0}\delta_{l'l_0'}Q(r,ll')+P_{ll_0}(r,l'l_0'), \tag{37}$$

and we assume that $Q\gg P$. The solution to (34) may then be written as a power series in P. To first order in P it is

$$\Gamma(L,ll')=\frac{\delta_{l0}\delta_{l'L}}{Q(R,ll')}-\frac{P_{l0}(R,l'L)}{Q(R,ll')Q(R,0L)}. \tag{38}$$

Then an evaluation of the right side of (36) only keeping terms linear in P yields

$$\frac{1}{V}\sum_\alpha\langle\phi_s\rangle\biggl[p_s^2+\frac{3}{R^2}\biggl(-1+\frac{RQ'(R,0l')}{Q(R,0l')}\biggr)-\frac{3\alpha}{R^4}\biggr]\tfrac{4}{3}\pi R^3, \tag{39}$$

since P is defined to be off-diagonal. Thus there is only virtual coupling of medium states by electrons in this approximation.

For short-range potentials or large enough R, the asymptotic form (28) can be used for a straightforward evaluation of (39). The result for this case is analogous to Eq. (11) except that allowance must be made for the fact that the M.P. can be in any rotational state. The result is

$$[E_s-U(r)+\nabla^2]\langle\phi_s(r)\rangle$$
$$=-4\pi\rho\biggl[\sum_{l'}f_s(l')\frac{K_{0l',0l'}}{p_{l'}}+\frac{\alpha}{R}\biggr]\langle\phi_s(r)\rangle, \tag{40}$$

where $f_s(l')$ is the fraction of the M.P. in the rotational state l' in the medium state s. Equation (40) is similar to (12) and to lowest order in ρ we get the total eigenvalue

$$E_{nls}=-\frac{1}{n^2}+\Delta\mathcal{E}+\mathcal{E}_s$$
$$-4\pi\rho\sum_{l'}f_s(l')\biggl[\frac{K_{0l',0l'}}{p_{l'}}\biggr]_{nl}-\frac{4\pi\alpha\rho}{R}, \tag{41}$$

where $[\ ]_{nl}$ indicates the average over the hydrogenic state (n,l). (Remember that p_l and consequently K are dependent upon r.) If we neglect the coupling of different rotational states of the M.P. by the electron [as we have already done in solving (34)], then the M.P. states will not change during the experiment and the term $\mathcal{E}_s$ will not contribute to the shift of the spectral line even though it will shift the individual levels. Thus the term $\mathcal{E}_s$ may be dropped in the approximation. The result for the relevant level shift is then

$$\Delta E_{nl,s}=\Delta\mathcal{E}-4\pi\rho\sum_{l'}f_s(l')\biggl[\frac{K_{0l',0l'}}{p_{l'}}\biggr]_{nl}-\frac{4\pi\alpha\rho}{R}, \tag{42}$$

and upon forming an ensemble average over medium states $f_s(l')$ is replaced by $f(l',T)$ in (41). Here $f(l',T)$ is the average fraction of the M.P. in state l' when the medium has a temperature T;

$$f(l',T)=(2w/kT)(2l'+1)\exp(-w/kT), \tag{43}$$

where the rotational eigenvalue is taken as $w(l')=wl'(l'+1)$.

---

[10] See, for instance, K. Takayanagi and S. Geltman, Phys. Rev. **138**, A1003 (1965). Note the difference in energy units there.

[11] Polar molecules have a sufficiently long-range potential ($\sim r^{-2}$) that restrictions analogous to (15) would appear to eliminate the possibility of using this type of formalism for interesting densities.

For homonuclear molecules,[11] the long-range potential takes the form[10]

$$V(r;\hat{q})=-\alpha/r^4-(2Q/r^3+\alpha'/r^4)P_2(\hat{r}\cdot\hat{q})\,, \qquad (44)$$

where

$$\begin{aligned}\alpha&=\tfrac{1}{3}(\alpha_{11}+2\alpha_{\perp})\,,\\ \alpha'&=\tfrac{2}{3}(\alpha_{11}-\alpha_{\perp})\,,\end{aligned} \qquad (45)$$

and Q is the electric quadrupole moment of the molecule. We must therefore find the modification of the radial wave functions $u_{00}(r,l'l')$ due to the presence of the potential (44) and the modified effective-range formula just as was done in order to arrive at (17). As in Sec. II, the distortion of the wave function by the long-range central part of the potential just cancels the last term in (39). (The distortions due to the noncentral potentials are higher order in R^{-1}.) The remaining contribution is the modification of the low-energy amplitude due to the long-range potentials. O'Malley[12] has given a discussion of this modified multichannel effective range formula. However, his derivation starts from his Eq. (3.3) which was first given by Spruch.[13] This equation is incorrect.[14] We have therefore given a brief description of the modification of $K_{0l',0l'}$ caused by the potential in (40) in Appendix B. The result is

$$K_{0l',0l'}/p_{l'}=-A_{00}(l')-\tfrac{1}{3}\pi\alpha p_{l'}\\ -\tfrac{4}{3}A_{00}(l')\alpha p_{l'}^2\ln(\tfrac{1}{4}p_{l'}\alpha^{1/2})\,. \qquad (46)$$

The resultant modification of the energy shift, (42), is

$$\Delta E_{nl}=\Delta\mathcal{E}+4\pi\rho\sum_{l'}f(l',T)[A_{00}(l')+\tfrac{1}{3}\pi\alpha(p_{l'})_{nl}\\ +\tfrac{4}{3}A_{00}(l')\alpha(p_{l'}^2\ln(\tfrac{1}{4}p_{l'}\alpha^{1/2}))_{nl}]\,. \qquad (47)$$

This is hardly different from the spherically symmetric case. In order to emphasize the possible differences one would return to (42) (with the last term removed because of the long-range distortion of the wave function) and put in an explicit form for the elastic scattering from the molecule, including p dependence. What is probably a more interesting problem is to return to (34) and obtain a solution by including the coupling between rotational states of the molecule due to interaction with the electron. To that end we briefly discuss the model of a molecule with only the rotational states $l'=0$, 2. Inclusion of $l'=1$ is trivial since it does not couple to either $l'=0$, 2. Equation (34) for Γ can now be solved explicitly. All Γ's for $L>2$ vanish. Omitting the details, the result which enters into (36) is

$$\left.\frac{\partial\psi_\alpha}{\partial r}\right|_{r=R}=-\frac{1}{R}\sum_s s\rangle\langle\phi_s\rangle+\sum_{s\alpha}s_\alpha\rangle\left\{00\rangle\langle\phi_{s\alpha,0}\rangle\frac{N_2}{D_2}\right.\\ \left.+\sum_{m'}|2m'\rangle\langle\phi_{s\alpha,2m'}\rangle\frac{N_3}{D_3}\right\}\,, \qquad (48)$$

where

$$N_2=\begin{vmatrix}u_{00}{}^{(0)\prime}(00) & u_{02}{}^{(0)\prime}(02)\\ u_{20}{}^{(0)}(20) & u_{22}{}^{(0)}(22)\end{vmatrix}\,, \qquad (49a)$$

$$N_3=\begin{vmatrix}u_{02}{}^{(2)\prime}(20) & u_{00}{}^{(2)\prime}(22) & u_{02}{}^{(2)\prime}(22)\\ u_{22}{}^{(2)}(00) & u_{20}{}^{(2)}(02) & u_{22}{}^{(2)}(02)\\ u_{22}{}^{(2)}(20) & u_{20}{}^{(2)}(22) & u_{22}{}^{(2)}(22)\end{vmatrix}\,. \qquad (49b)$$

Here the u's are the radial wave functions of (27), with $r=R$ and the R dependence suppressed. The prime means a derivative with respect to R. The previously suppressed dependence of u upon L has been made explicit as a superscript. The determinants D_2 and D_3 can be gotten from N_2 and N_3, respectively, by removing the primes on u in the first rows. If (48) is inserted into (36), the sum on α performed and the ensemble average taken, the result is

$$[E_s-U(r)+\nabla^2]\langle\phi_s\rangle=\tfrac{4}{3}\pi\rho R^3\left\{p_s{}^2-\frac{3}{R^2}\right.\\ \left.+\frac{3}{R}\left(\frac{N_2}{D_2}f(0,T)+\frac{N_3}{D_3}f(2,T)\right)\right\}\langle\phi_s\rangle\,. \qquad (50)$$

The effect of the coupling appears on the right side of (50) through the ratios N/D. It also appears on the left through the eigenvalue E_s, which contains the energy of the medium. If the process of exciting the absorbing atom does not change the medium state (as is true in processes not involving intense coherent radiation), then this dependence may be dropped in the same way as was discussed in connection with (42).

The N/D terms in (50) are rather complicated functions of p^2 and the K matrix. Expansion is possible through the inequality $pR\ll 1$, but because of the large cross sections involved even at these low energies the inequality $pR\gg K$ may not hold. In that case the simple multiple-scattering method used here fails, the reason being that the cross sections are large enough so that the electron "sees" overlapping M.P. In the case where the inequality $pR\gg K$ holds, expansion of the determinants leads to a result for the right side of (50) which is

$$-4\pi\rho(f(0,T)K_{00,00}/p_0+f(2,T)K_{02,02}/p_2)\,,$$

which is essentially the result of (40) (with the distortion terms α/R removed.) Thus we may conclude from the model that when our method works, the result (42) (with the distortion term removed) is general.

APPENDIX A

Modifications due to a polarization potential [Eq. (14)].

---

[12] T. F. O'Malley, Phys. Rev. **134**, A1188 (1964).

[13] L. Spruch, in *Lectures in Theoretical Physics*, edtied by W. E. Brittin, B. W. Downs, and J. Downs (Interscience Publishers Inc., New York, 1962), Vol. 4.

[14] L. Spruch (private communication).

The integral equation for the s-wave radial wave function can be written

$$u(r)=\sin(pr+\delta)-\frac{1}{p}\int_r^\infty dr' \sin p(r-r')v(r')u(r'), \quad \text{(A1)}$$

which for large r is approximated by

$$u(r)=\sin(pr+\delta)-\frac{1}{p}\int_r^\infty dr' \sin p(r-r')v(r')$$
$$\times\sin(pr'+\delta)=\sin(pr+\delta)-\alpha\cos(pr+\delta)/6pr^3$$
$$+(2p)^2\alpha[\sin(pr-\delta)S(2pr)+\cos(pr-\delta)C(2pr)]. \quad \text{(A2)}$$

Here we define

$$\begin{pmatrix} C(x) \\ S(x) \end{pmatrix}=\int_x^\infty \frac{dy}{y^4}\begin{pmatrix} \cos y \\ \sin y \end{pmatrix}. \quad \text{(A3)}$$

The new terms on the right side of (11) may then be written

$$\langle\psi\rangle\frac{2\pi R^2\rho\alpha}{\sin^2(pR+\delta)}\left\{\frac{1}{3R^3}-(2p)^3[(\cos 2\delta)C(2pR)\right.$$
$$\left.-(\sin 2\delta)S(2pR)]\right\}, \quad \text{(A4)}$$

where only the lowest-order terms in α have been retained. We now proceed as before with the inequalities

$$pR<1,$$
$$pR>\tan\delta, \quad \text{(A5)}$$

yielding $\langle\psi\rangle 4\pi\rho\alpha/R$ for this contribution. The other modification comes from the change in the effective-range expansion which for r^{-4} potentials can be written[8]

$$\tan\delta/p=-A-\tfrac{1}{3}\pi\alpha p-\tfrac{4}{3}\alpha A p^2\ln(p\tfrac{1}{4}\alpha^{1/2})+O(p^2). \quad \text{(A6)}$$

This yields an additional term to the right side of (11) of the form

$$[\tfrac{4}{3}\pi^2\alpha\rho p+(16\pi/3)\alpha A p^2\ln(p\tfrac{1}{4}\alpha^{1/2})]\langle\psi\rangle. \quad \text{(A7)}$$

APPENDIX B: MODIFIED MULTICHANNEL EFFECTIVE-RANGE EXPANSION

Our starting point is Eq. (27) for the radial wave functions $u_{ll_0}(r,l'l_0')$. Using the long-range potential, Eq. (44), the right side of (27) can be written

$$\sum_{\lambda\lambda'} v_{ll',\lambda\lambda'}(r)u_{\lambda l_0}(r,\lambda' l_0'), \quad \text{(B1)}$$

where for large r

$$v_{ll',\lambda\lambda'}(r)=-(\alpha/r^4)\delta_{l\lambda}\delta_{l'\lambda'}-(2Q/r^3+\alpha'/r^4)$$
$$\times\langle LMll'|P_2|LM\lambda\lambda'\rangle. \quad \text{(B2)}$$

Zemach[15] has given a more convenient form of (27). For our purposes it may be written

$$K_{qq',l_0l_0'}(r)=K_{qq',l_0l_0'}(R)-(p_{q'}p_{l_0'})^{1/2}\sum_{ll'\lambda\lambda'}\int_{\Delta R}^{\Delta r}x^2dx$$
$$\times[\delta_{lq}\delta_{l'q'}j_l(ax)-n_l(ax)K_{qq',ll'}(x/\Delta)(p_{q'}/p_{l'})^{1/2}]$$
$$\times v_{ll'\lambda\lambda'}(x/\Delta)[\delta_{\lambda l_0}\delta_{\lambda' l_0'}j_\lambda(x/a)-n_\lambda(x/a)$$
$$\times K_{\lambda\lambda',l_0l_0'}(x/\Delta)(p_{\lambda'}/p_{l_0'})^{1/2}], \quad \text{(B3)}$$

where $a=(p_{l'}/p_{\lambda'})^{1/2}$ and $\Delta=(p_{l'}p_{j'})^{1/2}$. Here $K(r)$ is the amplitude which would result from the potential $v(r)$ truncated at r. R is chosen to be some fixed value large enough for (B2) to be used in (B3). Equation (B3) is similar to an equation used by Levy and Keller[16] for deriving a modified effective-range theory for single-channel scattering and their method may be used here. The method consists of an iteration procedure of replacing K on the right side of (B3) by the previous iteration. The zeroth order is just given by the first term on the right. A clear discussion of the reason that the procedure works is given by O'Malley.[12,17] The first-order term is obtained by replacing K by K^0 under the integral. $K^{(0)}$ results from the scattering from a short-range potential, so that[18]

$$K_{qq',ll'}{}^{(0)}(R)=p_{q'}{}^{q+\frac{1}{2}}p_{l'}{}^{l+\frac{1}{2}}A_{ql}{}^{(0)}(R), \quad \text{(B4)}$$

where A is a generalization of the scattering length. A straightforward evaluation of the integrals for small p yields

$$K_{0l',0l'}{}^{(1)}/p=-A_{00}{}^{(1)}-\tfrac{1}{3}\pi\alpha p_{l'}$$
$$-\tfrac{4}{3}A_{00}{}^{(0)}\alpha p_{l'}{}^2\ln(p_{l'}\tfrac{1}{4}\alpha^{1/2})+O(p_{l'}{}^{l}). \quad \text{(B5)}$$

Here, as O'Malley[12] points out in the spherically symmetric case, $A_{00}{}^{(1)}$ is the perturbation correction to $A_{00}{}^{(0)}$, and so the entire result (to this order in p) can be obtained by dropping the superscripts on the A's. Actually, $A_{00}{}^{(1)}$ is slowly dependent upon energy through terms like

$$\sum_{qq'\lambda\lambda'}\frac{\alpha_{qq',\lambda\lambda'}}{q+\lambda+3}\frac{p_{l'}}{p_{q'}},$$

with additional factors. However, at the energy in question here the ratio of these momenta are not significantly different from unity, so that no further expansion is necessary. The result (B5) is seen to be essentially the same as for the spherically symmetric case.

---

[15] C. Zemach, Nuovo Cimento 33, 939 (1964).

[16] B. R. Levy and J. B. Keller, J. Math. Phys. 4, 54 (1963).

[17] Note that the r^{-3} part of (B2) is not as effective a central r^{-3} potential since the matrix element multiplying it in (B2) vanishes for $l=\lambda=0$ and $l+\lambda=1$, which are the terms which would otherwise dominate in our expansion.

[18] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, Ltd., London, 1958).