Environmental effects on atomic energy levels[†]

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This paper considers environmental effects both on the ground-state charge distribution and on the different energy levels of a hydrogen atom. The medium is represented by a continuous dielectric, and the effect of the polarization of this medium is computed, using both a simplified self-consistent-field variational treatment, and also a perturbation calculation. The dielectric effects of the medium are compared with similar results based on discrete molecular models, taking into account both dispersion and overlap-repulsion forces. The dielectric effects on the ground-state charge distribution are of the same order of magnitude as the effects due to dispersion forces. The dielectric effects on Rydberg-type electronic transitions lead to blue shifts. This conclusion is in agreement with some recent experimental results.

1. INTRODUCTION

The perturbation of the energy levels of an atom or a molecule by a compressed gas, a solvent or a solid can in certain cases by treated by the use of a continuous dielectric model for the surrounding medium [1, 2]. One condition for the adequacy of this treatment must be that the penetration of the charge of the trapped atom into the medium is sufficiently great as to make the bulk properties of the medium applicable. This approach, using bulk properties, is based on the assumption that the perturbing effect of the medium is mainly due to long-range interactions.

Several related phenomena are involved. Thus the presence of the surrounding medium affects the charge distribution of a trapped hydrogen atom—a situation that can be investigated experimentally by the use of electron-spin and nuclear magnetic resonance techniques [3, 4]. Further, a study of environmental effects on the energies of optical absorption frequencies yields information concerning the relative shifts of two distinct energy levels, when the nuclear configuration is always that of the ground state of the system. Finally, the dielectric medium model may be applicable for Rydberg-type transitions in the ultra-violet, when excitation of a bound electron causes a considerable change in the overlap of the charge-cloud with the medium. When it is realized that for a hydrogen atom the mean radius in a state of principal quantum number n is almost proportional to n^2, it is clear that Rydberg transitions would be expected to show this effect in a pronounced manner.

In the present work we consider environmental effects on the charge distribution and excitation energy of a trapped atom, here taken to be hydrogen.

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Application of the continuum model will involve a semi-empirical reduction of a complicated many-electron problem to a one-electron problem. We shall conclude with a comparison of the results predicted by a dielectric model with those due to dispersion and short-range repulsion forces.

2. Application of dielectric model to the ground state

To simplify the calculations we consider the environmental perturbation of the energy levels of atomic hydrogen. Our model (figure 1) is that of an *H* atom located at the centre *O* of a spherical cavity of radius R_0 in a continuous dielectric. The properties of this medium are specified by its static dielectric constant D_S and its optical dielectric constant D_{op}. This latter is the high-frequency dielectric constant, corresponding to frequencies higher than those of the nuclear vibrations. The problem of the interaction energy between an additional electron and a dielectric medium has already been treated in relation to electron trapping in the solid [5, 6, 7] and liquid states [8, 9].

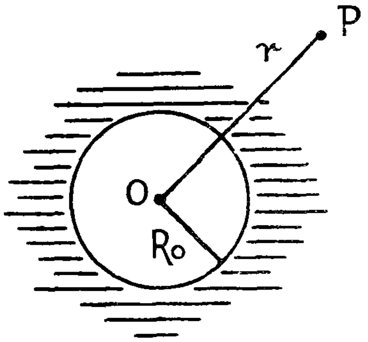

Figure 1. Model of dielectric medium, shown shaded, with atom at centre of cavity of radius R_0.

We start with the interaction between the electron, the H nucleus, and the medium polarization. As a result of the polarization induced by the field of the moving electron, the unperturbed electron-nucleus interaction $v(r) = -1/r$ (in which we use atomic units of charge and mass and length) will be diminished by the medium. For $r > R_0$ the nuclear charge contributes $-1/D_S \, dv(r)/dr$ to the electrostatic field. Also the polarization field of the medium is $(1 - 1/D_S) \, q(r)/r^2$, where

$$q(r) = \int_0^r |\psi(r)|^2 \, d\tau \tag{1}$$

is the fraction of charge within a radius r, and $\psi(r)$ is the wave function of the valence electron in the ground state. Here and later we are assuming spherical symmetry.

Thus the total field acting on the electron in the 1s-state is derived from a potential $V_{1s}(r)$, where

$$-\text{grad } V_{1s}(r) = -\frac{1}{D_S} \frac{dv(r)}{dr} + \alpha_S \frac{q(r)}{r^2} \tag{2}$$

with the abbreviation, which we shall frequently use:

$$\alpha_{\mathrm{S}} = 1 - \frac{1}{D_{\mathrm{S}}}. \tag{3}$$

Integrating (2) with the condition that $V_{1\mathrm{s}}(\infty) = 0$, we have

$$V_{1\mathrm{s}}(r) = -\frac{1}{D_{\mathrm{S}} r} - \alpha_{\mathrm{S}} \int_r^\infty q(r) r^{-2} \, dr. \tag{4}$$

Assuming continuity of $V_{1\mathrm{s}}(r)$ at $r = R_0$, and setting

$$p(r) = 1 - q(r) = \int_r^\infty |\psi(r)|^2 \, dr, \tag{5}$$

we obtain the final expression

$$\begin{aligned} V_{1\mathrm{s}}(r) &= -\frac{1}{r} + \alpha_{\mathrm{S}} \int_r^\infty p(r) r^{-2} \, dr, \quad r > R_0 \\ &= -\frac{1}{r} + \alpha_{\mathrm{S}} \int_{R_0}^\infty p(r) r^{-2} \, dr, \quad r < R_0. \end{aligned} \tag{6}$$

The Schrödinger equation may now be written down. It is an integro-differential equation since the potential energy function $V_{1\mathrm{s}}(r)$ itself involves the wave function according to (5) and (6). This eigenvalue problem may be solved by a restricted form of variational self-consistent-field technique [1, 7]. If we begin with the one-parameter wave function

$$\psi_0(r) = \sqrt{\frac{\mu^3}{\pi}} \exp(-\mu r), \tag{7}$$

where μ is yet to be determined, we soon calculate from (5) that

$$p(r) = (1 + 2\mu r + 2\mu^2 r^2) \exp(-2\mu r). \tag{8}$$

Then, by use of (6), and dropping the suffix 1s for the moment,

$$\begin{aligned} V(\mu, r) &= -\frac{1}{r} + \alpha_{\mathrm{S}} \frac{(1 + \mu r) \exp(-2\mu r)}{r}, \quad r > R_0 \\ &= -\frac{1}{r} + \alpha_{\mathrm{S}} \frac{(1 + \mu R_0) \exp(-2\mu R_0)}{R_0}, \quad r > R_0. \end{aligned} \tag{9}$$

The wave equation is

$$\mathscr{H} \psi = E \psi,$$

where

$$\mathscr{H} = -\tfrac{1}{2} \nabla^2 + V(\mu, r). \tag{10}$$

We solve this equation variationally, putting

$$\psi = \psi_1(r) = \sqrt{\frac{\lambda^3}{\pi}} \exp(-\lambda r) \tag{11}$$

and choosing λ so that

$$\frac{\partial}{\partial \lambda} \int \psi_1^* \mathscr{H} \psi_1 \, d\tau = 0. \tag{12}$$

Self-consistency is now achieved by choosing μ in (7) so that the corresponding value of λ determined from (12) is such that $\lambda = \mu$. This gives the following equations to determine λ and E:

$$\lambda = 1 - \alpha_{\mathrm{S}} \left(\tfrac{11}{16} + \tfrac{11}{4} X + \tfrac{7}{2} X^2 + 2X^3 \right) \exp(-4X), \tag{13}$$

$$E(\lambda)=\tfrac{1}{2}\lambda^2-\lambda+\frac{\alpha_S}{R_0}\{(1+X)\exp(-2X)-(1+\tfrac{21}{8}X+\tfrac{5}{2}X^2+X^3)\exp(-4X)\} \quad (14)$$

in which $X=\lambda R_0$ and, as before, $\alpha_S=1-1/D_S$.

More refined calculations could be made, choosing more complicated and flexible functions than the simple exponential (7). We have not made them, since although they would lead to a more accurate wave function and energy, it is most unlikely that they would significantly alter our main conclusions.

The special case of $R_0=0$ is of some interest. It corresponds to the ' interstitial ion ' model, formerly treated using a somewhat different approach [7, 9]. Our present treatment leads to the results:

$$\lambda=1-\tfrac{11}{16}\alpha_S, \quad E(\lambda)=\tfrac{1}{2}\lambda^2-\lambda+\tfrac{3}{8}\alpha_S\lambda. \quad (15)$$

The reference state in this system is a free electron located at infinite distance from the cavity, while the medium is polarized and produces the potential given by equation (6).

An alternative method of getting the same results as in (6)–(14) is to use the general expression for the total energy W of the system consisting of dielectric medium plus trapped H atom.

$$W=\int\psi^*(r)\left\{-\tfrac{1}{2}\nabla^2-\frac{1}{D_S r}\right\}\psi(r)d\tau-\frac{\alpha_S}{8\pi}\int\mathbf{D}_e{}^2\,d\tau, \quad (16)$$

where the dielectric displacement vector $\mathbf{D}_e$ satisfies

$$\operatorname{div}\mathbf{D}_e=4\pi\,|\psi(r)|^2, \quad (17)$$

and then solving the variational problem

$$\delta W=0 \text{ for all } \delta\psi \text{ such that } \int\psi^*\psi\,d\tau=1.$$

3. Perturbation of the ground-state energy

Let us define the perturbation energy of the ground state due to the dielectric medium as the energy change

$$\Delta E(1s)=E_H(1s)-E(\lambda), \quad (18)$$

where $E_H(1s)$ is the energy of an isolated hydrogen atom in its ground state, and $E(\lambda)$ is given by (14) using the value of λ given by (13).

The dependence of $\Delta E(1s)$ on the parameter α_S is shown in figure 2. Dielectric effects appear to decrease the binding energy. For the ground state this effect decreases sharply with increasing R_0, and obviously depends on the total amount of the valence electron charge-cloud that penetrates into the medium. This effect is qualitatively similar to the effect of short-range repulsion forces between two ground-state hydrogen atoms. A comparison of the two energies is of some interest. It is well known [10, 11] that the interaction energy of two H atoms with randomly oriented spins can be estimated by using the concept of pseudo-valence forces. This mutual energy $E(R)$, at separation R, is

$$E(R)=\tfrac{1}{4}\,{}^1E(R)+\tfrac{3}{4}\,{}^3E(R), \quad (19)$$

where ${}^1E(R)$ is the energy of the lowest ${}^1\Sigma_g$ state of the H_2 molecule, and ${}^3E(R)$ is the energy of the lowest ${}^3\Sigma_u$ state. The use of spectroscopic data [17] for these two states yields the values presented in table 1.

In order to obtain the total interaction energy by this means, the mutual pair energy shown in the table should be multiplied by the number of nearest neighbour atoms Z. Thus in a face-centred cubic-solid there are three possible sites [3]: a substitutional site for which $Z=12$, an octahedral site for which $Z=6$, and a tetrahedral site for which $Z=4$. Other situations can be dealt with similarly.

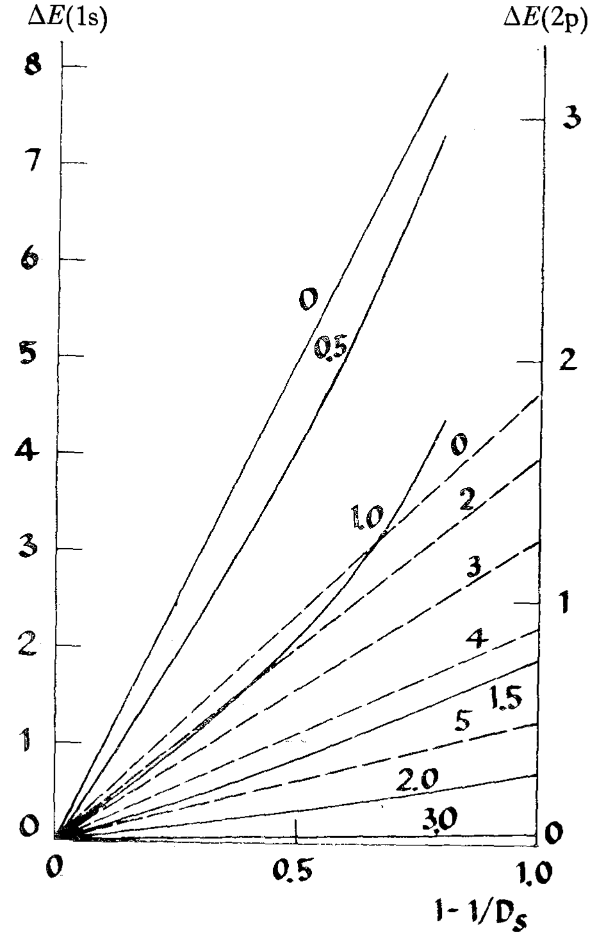

Figure 2. The dielectric effect on the energy levels of a hydrogen atom: Solid curves: the effect of the energy on the 1s ground state, calculated by the variation method; dashed curves: the effect on the energy of the 2p excited state, calculated by the perturbation method. Energies are in eV.

R and $2R_0$ (a_0)	$E(R)$ (ev)	$\Delta E(1s)$ (ev)
3	0·123	0·862
4	0·0268	0·326
6	0·000628	0·044
8	−0·000395	0·006

Table 1. Interaction energies for the ground state of H, using spectroscopic data ($E(R)$) and the dielectric model ($\Delta E(1s)$) with $D_s=2$.

In comparing the values of $E(R)$ with the dielectric medium values $E(\lambda)$ the chief difficulties are (i) the number Z of neighbours involved in $E(R)$, and (ii) the unambiguous determination of the relation between R, the distance of the neighbour atom from the central atom, and R_0 the cavity radius. It seems reasonable to identify R_0 with one half the distance between the nuclei, setting

$$R_0 \simeq \tfrac{1}{2}R. \tag{20}$$

This is the relationship adopted in table 1. It appears from this table that, when allowance is made for the factor Z, the perturbation energies resulting from the dielectric model treatment are of the same order of magnitude for small distances as the short-range repulsion forces; but for larger distances the dielectric model yields larger long-range repulsion forces.

4. CHARGE DISTRIBUTION IN GROUND STATE

We have already stated that the unpaired electron-spin density at the proton can be experimentally measured [3, 4]. Such data have recently been applied [3] to the theoretical evaluation of the interaction of ground-state H atoms with rare gas matrices [4]. It is of interest, therefore to see what density is predicted by our continuum model. As we shall show, the dielectric effect leads to expansion of the charge-cloud of the unpaired electron.

This latter follows from (11) and (13), since

$$|\psi(0)|^2 = \frac{\lambda^3}{\pi} \quad \text{and} \quad \lambda < 1. \tag{21}$$

The relative change in the unpaired electron density at the nucleus is defined by

$$\rho \equiv \rho_d = \frac{|\psi(0)|^2 - |\psi_0(0)|^2}{|\psi_0(0)|^2} \tag{22}$$

where $|\psi_0(0)|^2 = 1/\pi$ is the unperturbed density. Thus the effect of the medium is to cause a relative change

$$\rho_d = \lambda^3 - 1. \tag{23}$$

Since $\lambda < 1$, ρ_d is negative.

We must now compare this with the results of the discrete molecular model. If, as we shall suppose, the medium is non-polar, so that ionic effects need not be taken into account, we shall have to include both dispersion forces and overlap repulsion forces. An approximate expression for the perturbed wave function of the system of two interacting H atoms can be obtained from the general—and accurate—expression {see, e.g. reference [12]} for the perturbed wave function by inserting in it the Unsöld approximation. In this we replace all energy level differences by an approximate mean excitation energy E_H. If the unperturbed wave function of the system is ϕ_0 and if ϕ is the corresponding perturbed wave function, and H' is the perturbation potential, then

$$\phi = \left\{1 + \frac{1}{2E_H}[H' - (H')_{00}] + \frac{1}{4E_H^2}[(H')^2 - (H'^2)_{00}]\right\}\phi_0. \tag{24}$$

For dispersion forces $(H')_{00}$, which is the mean-value of the perturbation potential in the ground state, vanishes identically.

Now the usual power-series expansion of H' shows that we may treat it as zero on each hydrogen nucleus. Thus the unpaired spin density at either nucleus is given by

$$|\psi(0)|^2=\left\{1-\frac{(H'^2)_{00}}{2E_H{}^2}\right\}|\psi_0(0)|^2 \tag{25}$$

correct to terms of the fourth order in H'. But the van der Waals interaction energy is given by

$$E_V=\frac{(H'^2)_{00}}{2E_H}.$$

Thus equation (25) shows that the contribution of dispersion forces to the relative change in spin density at the nucleus is

$$\rho_V=Z\left(-\frac{E_V}{E_H}\right). \tag{26}$$

It follows from (26) that the van der Waals forces cause a reduction in the charge density. Since the presence of these forces results in a partial excitation of the electron to higher energy levels, in which it is removed further from the nucleus, this reduction is not surprising. Our conclusions are similar to some results recently obtained by Adrian [4]. The main difficulties in relation both to the present treatment and that of Adrian, are (i) the doubt about the value of the coordination number Z, and (ii) the problem of the additivity of dispersion forces. These forces are additive in the approximation of second-order perturbation theory, which is as far as we have carried the analysis. But application of third-order perturbation theory does not lead to additive energies. It seems probable, however, that this error is not large in most cases of physical interest.

Short-range repulsion forces are caused by the overlap between the charge density of the trapped H atom and the charge distribution of the particles which constitute the medium. This effect can be approximately allowed for by orthogonalizing the wave function ψ_0 of the unpaired electron to the wave functions of all the other electrons ϕ_i of the medium. This is conveniently done by Schmidt's orthogonalization process. Thus, if ψ^{or} is the orthogonalized wave function corresponding to ψ_0, then

$$\psi^{or}=\frac{\psi_0-\sum_i S_i\phi_i}{\left(1-\sum_i S_i{}^2\right)^{1/2}} \tag{27}$$

in which S_i is the overlap integral $\langle\psi_0\,|\,\phi_i\rangle$. Equation (27) shows that ψ^{or} mixes into ψ_0 small parts of the wave functions of all the electrons of the medium having the same spin. If the overlap integrals are small the contributions from the ϕ_i are additive.

Let us consider the interaction of the trapped H atom with a second H atom. Then for relatively large separations R, the change in electron density at the nucleus due to these exclusion forces is

$$\rho_e=S^2-2S\exp(-R). \tag{28}$$

Since $\rho_e>0$ for large R, this means that exclusion forces increase the charge density at the nucleus.

The various relative effects—ρ_d, ρ_V, ρ_e—are shown in table 2. In this table the dielectric value ρ_d is calculated with $D_S=2$.

The results in this table indicate that, just as in the energy changes of table 1, the dielectric contribution to ρ is of the same order as that of the dispersion forces, and rather smaller than that of the overlap forces. But there are reasons for believing that our simple result (28) slightly over-emphasizes the exclusion effect. For in some practical applications [4] for rare gases and molecular matrices containing trapped H atoms, their contribution to ρ_e is smaller than in table 2.

R (or $2R_0$) in a_0	ρ_d	$(1/Z)\rho_v$	$(1/Z)\rho_e$
3	−0·081	−0·0164	0·0865
4	−0·021	−0·00296	0·0287
5	—	−0·000768	0·00794
6	−0·0027	−0·000257	0·00199

Table 2. Relative changes in spin density at the proton.

5. OPTICAL EXCITATION ENERGIES

Vertical electronic transitions are subject to the restrictions of the Franck–Condon principle. This requires that immediately after the excitation the nuclear configuration of the medium is the same as in the ground state, whereas the core electrons of the medium have adjusted themselves to the new field resulting from the excited-state charge distribution of the trapped atom. This latter is not spherically symmetrical, because allowed transitions will be of the form 1s→np. We ought therefore to deal with an effective potential more general than (9). This turns out to be rather complicated, so we shall make the assumption, entirely analogous to that usually made in atomic self-consistent field calculations, that the potential function V_e in the excited state is entirely spherically symmetrical. Without this simplification the problem of true self-consistence is almost insoluble.

So when calculating the wave function ψ_p and energy E_p in the excited state, we use the potential function (c.f. (4))

$$V_e(r) = -\frac{1}{D_s r} - \left(\frac{1}{D_{op}} - \frac{1}{D_s}\right)\int_r^\infty q_{1s}(r)\, r^{-2}\, dr \\ - \left(1 - \frac{1}{D_{op}}\right)\int_r^\infty q_p(r)\, r^{-2}\, dr, \quad r > R_0, \tag{29}$$

where the charge distribution q_p in the excited state is given, as in (1), by

$$q_p(r) = \int_0^r |\psi_p|^2\, 4\pi r^2\, dr. \tag{30}$$

The second term in (29) arises from the nuclei of the medium, whose polarization is still determined by the ground-state electron density; but the third term comes from the electronic polarization associated with the excited-state electron density.

We may write (29) in the form

$$r > R_0, \quad V_e(r) = -\frac{1}{r} + (\alpha_s - \alpha_{op})\int_r^\infty t^{-2}\, dt \int_t^\infty |\psi(1s)|^2\, d\tau \\ + \alpha_{op}\int_r^\infty t^{-2}\, dt \int_t^\infty |\psi_e|^2\, d\tau,$$

$$r<R_0,\quad V_{\mathrm{e}}(r)=-\frac{1}{r}+(\alpha_{\mathrm{s}}-\alpha_{\mathrm{op}})\int_{R_0}^{\infty} t^{-2}\,dt\int_{t}^{\infty}|\psi(1\mathrm{s})|^2\,d\tau+\alpha_{\mathrm{op}}\int_{R_0}^{\infty} t^{-2}\,dt\int_{t}^{\infty}|\psi_{\mathrm{e}}|^2\,d\tau, \qquad (31)$$

with

$$\alpha_{\mathrm{op}}=1-1/D_{\mathrm{op}},\qquad \alpha_{\mathrm{s}}=1-1/D_{\mathrm{s}}.$$

We have made some calculations for the 1s→2p transition, employing the perturbation technique proposed by Coulson and Brown [1], who showed that if we write

$$V_{\mathrm{e}}(r)=-\frac{1}{r}+V_{\mathrm{pert}},$$

then we may calculate V_{pert} on the supposition that in the integrations of (31) ψ_{e} is given its unperturbed form, and then use V_{pert} as a perturbation. For reasonable values of the cavity radius R_0 the resulting error was small, and almost certainly much smaller than that due to inadequacies in the whole model.

We choose for ψ_{e} the normalized one-parameter radial wave function

$$\psi_{2\mathrm{p}}=\left(\frac{\nu^5}{3\pi}\right)^{1/2} r\exp(-\nu r)\quad\text{with}\quad \nu=\tfrac{1}{2}. \qquad (32)$$

The perturbation potential V_{pert} due to the medium becomes

$$V_{\mathrm{pert}}(r)=(\alpha_{\mathrm{s}}-\alpha_{\mathrm{op}})\frac{1+\lambda r}{r}\exp(-2\lambda r)+\alpha_{\mathrm{op}}\frac{1+\frac{3}{2}\nu r+\nu^2r^2+\frac{1}{3}\nu^3r^3}{r}\exp(-2\nu r) \qquad (33)$$

for $r>R_0$. The value for $r<R_0$ is obtained from (33) by simply putting $r=R_0$ in the formula. Thus the perturbation energy is

$$\Delta E(2p)=\int_0^{R_0}|\psi_{2\mathrm{p}}|^2V_{\mathrm{pert}}(R_0)\,d\tau+\int_{R_0}^{\infty}|\psi_{2\mathrm{p}}|^2V_{\mathrm{pert}}(r)\,d\tau. \qquad (34)$$

Numerical calculations using this formula have been carried out for a non-polar, medium, and are shown in figure 2 for various values of the cavity radius R_0 and for $1-1/D_{\mathrm{s}}$ varying from 0 to 1 and with $D_{\mathrm{op}}=D_{\mathrm{s}}$. The environmental effect on the transition energy $\Delta E_{\mathrm{trans}}$ is obtained from

$$\Delta E_{\mathrm{trans}}=\Delta E(1\mathrm{s})-\Delta E(2\mathrm{p}). \qquad (35)$$

The dependence of $\Delta E_{\mathrm{trans}}$ on R_0 for $D_{\mathrm{s}}=D_{\mathrm{op}}=2$ is given in figure 3. This shows that for relatively large R_0 the medium exerts a larger influence on the excited state than on the ground state. There is a blue shift for $R_0>1{\cdot}5a_0$.

6. HIGHER EXCITED STATES AND PHOTOIONIZATION

We have treated the problem of higher excited states by considering a non-polar medium for which $D_{\mathrm{s}}=D_{\mathrm{op}}$, and so $\alpha_{\mathrm{s}}=\alpha_{\mathrm{op}}$. In this case the second terms in (31) vanish identically, so that (31) is effectively the same as (6). This implies that, unlike the situation when $\alpha_{\mathrm{s}}\neq\alpha_{\mathrm{op}}$, there is no subsequent relaxation of the medium polarization, following the vertical excitation. We may therefore say that the energies of the vertical and equilibrium transitions are the same.

It is not easy to decide on suitable wave functions ψ_{e} for the excited states, though we still adhere to the approximation of spherical symmetry. But probably good insight will be obtained if we adopt Slater-type atomic orbitals.

These are defined by

$$\psi_e = N r^{n-1} \exp(-cr), \quad c = 1/n, \quad N^2 = \frac{(2/n)^{2n+1}}{4\pi(2n)!}. \tag{36}$$

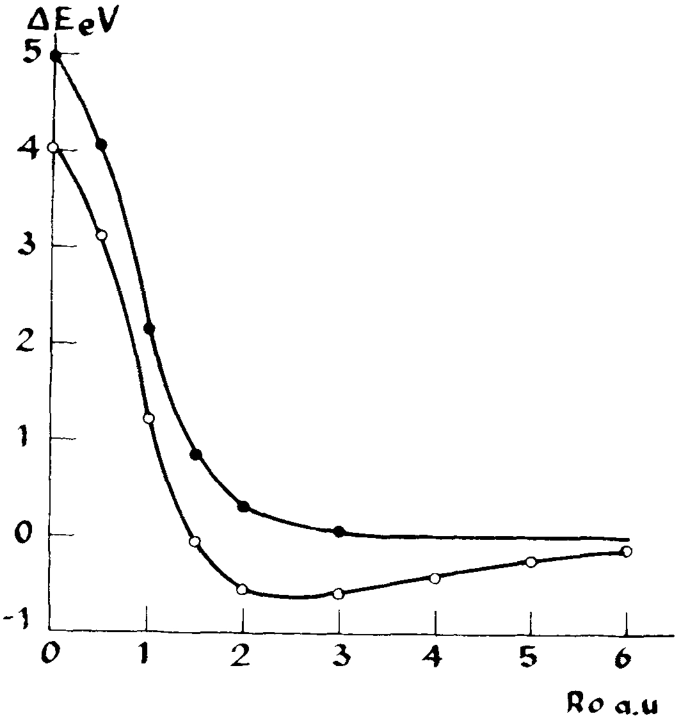

Figure 3. The dielectric effect on optical transition energies when $D_s = D_{op} = 2$. Open circles: transition 1s→2p; full circles: photoionization process from the ground state.

This leads to

$$V_{np}(r) = -\frac{1}{r} + \alpha_{op}\int_r^\infty p(t)t^{-2}\,dt, \quad r > R_0 \tag{37}$$

with

$$p(t) = \exp(-2ct)\left\{1 + \sum_{j=1}^{2n-1}\frac{(2ct)^{2n-j}}{(2n-j)!}\right\}. \tag{38}$$

For $r < R_0$, the lower limit r in the integral of (37) is replaced by R_0. In the limiting case as $n \to \infty$, $p(t) \to 1$ and the potential function reduces to the simple form

$$\begin{aligned} V_{np}(r) &= -\frac{1}{r} + \frac{\alpha_{op}}{R_0}, \quad r > R_0 \\ &= -\frac{1}{D_{op}r}, \quad r > R_0. \end{aligned} \tag{39}$$

This particular potential function (39) has been used earlier by Reiss [13] to study the ionization processes of atoms trapped in silicon and germanium. If we adopt the first-order perturbation approximation, this potential (39) leads to an energy change ΔE given by

$$\Delta E = \frac{\alpha_{op}}{R_0}\left[1 - \exp(-2cR_0)\left\{1 + \sum_{j=1}^{2n-1}\frac{j(2cR_0)^{2n-j}}{2n.(2n-j)!}\right\}\right]. \tag{40}$$

We have made a comparison of the energy changes predicted by Reiss' model, using the approximate potential (39), and the complete dielectric treatment, in which the polarizing effect of the valence electron is taken into account. It is not worth while to report these calculations in detail. Their conclusion is that the approximate potential (39) seriously overestimates polarization effects in the medium when the atom is in its ground and first few excited states. Thus the use of a potential which does not incorporate the polarization of the dielectric by the central electron appears not to be justified.

Our treatment based on the dielectric model, and taking account of the polarization of the medium by the centrally bound electron, indicates that the energy of a vertically excited state is determined partly by the charge distribution in this excited state. But for the potential well which is represented by equation (37) when $n \to \infty$, the binding energy in the excited state is zero. Thus the changes in photoionization energy will depend upon the environment, through its influence on the ground state. This influence is shown graphically in figure 3.

7. COMPARISON WITH OTHER EFFECTS ON THE EXCITATION ENERGY

We shall now return to a more complete discussion of the dispersion energy effect upon optical transitions. It is well known that dispersion forces usually lead to red spectral shifts [14, 15]. This is because the interaction energy between the trapped atom or molecule in its excited state and the medium is usually higher than in the ground state, leading to a displacement of the electronic transition energy to longer wavelengths. Unfortunately any accurate treatment of dispersion forces between an atom in a Rydberg-type excited state and another atom in its ground state is complicated by the fact that the interaction forces are not strictly spherically symmetrical. However, Margenau [21] has derived an appropriate expression for this interaction potential. He shows that it is positive if the mean excitation energy of the perturbing atom is smaller than the excitation energy of the trapped atom. In that case dispersion forces will lead to a blue shift.

An alternative to the use of Margenau's formula is to estimate the interaction energy using Buckingham's expression [16] for the dispersion force energy E_{V} between two atoms A and B in any chosen states a distance R apart. The formula is

$$E_v = -\frac{4a_0^2}{9R^6} \sum_{i=1}^{n_a} \sum_{j=1}^{n_b} \frac{(\overline{r_i^2})^2(\overline{r_j^2})^2}{\overline{r_i^2}+\overline{r_j^2}}, \tag{41}$$

where n_a and n_b are the total numbers of electrons in the interacting atoms, and r^2 is the mean-square radius for an atomic orbital. For Slater orbitals (16)

$$\overline{r^2} = \tfrac{1}{4}n^2(2n+1)(2n+2)a_0^2. \tag{42}$$

For the case of two hydrogen atoms however there is no difficulty in calculating the necessary polarizabilities to use in the conventional London expression. We show in table 3 a comparison between the spectral shift ΔE_{d} due to dielectric medium polarization (for the case of $D_{\mathrm{op}} = D_{\mathrm{s}} = 2$) and the dispersion shift ΔE_v. This is given per neighbour, and so requires to be multiplied by the number of nearest-neighbour atoms to the trapped one. Red shifts are represented in this table by a positive sign, and blue shifts by a negative one

This table indicates that at relatively small distances (up to $6a_0$) the red shift due to van der Waals' forces is numerically of the same order of magnitude as the blue shift due to dielectric polarization. But at larger distances the dielectric effect is appreciably higher.

R(or $2R_0$) (a_0)	ΔE_d (ev)	ΔE_v (ev)
4	−0·551	−0·692
5	−0·570	0·179
6	−0·592	0·0619
8	−0·443	0·0106
10	−0·251	0·0028

Table 3. Comparison of spectral shifts caused by dielectric effect (ΔE_d) and dispersion forces (ΔE_v) for a 1s→2p transition†.

The effects of overlap forces on the transition energy have been treated in some detail by Coulson and Polansky [2, 18] on the basis of a perturbation model. These results, which are as yet not fully published, predict a blue shift at relatively small distances (for which $R < 4a_0$).

8. EXPERIMENTAL EVIDENCE FOR LONG-RANGE REPULSION FORCES

It appears from the foregoing analysis that dielectric effects may lead to blue shifts caused by long-range interactions, and that these are too high to be attributed to short-range repulsion forces. Some experimental data seem to confirm this conclusion. Thus blue spectral shifts have been obtained for benzene and for the ^1L_b transition of naphthalene, when perturbed by helium at high pressures [19]. These effects could not be attributed to dispersion forces which are higher for the excited state of benzene than for the ground state, when it is interacting with helium. They were therefore assigned to long-range repulsive forces.

Blue shifts have also been observed [20, 22] for the $Hg^1S_0 \rightarrow {}^3P_1$ transition in the gas phase, when induced by He and by H_2 at high pressures. Originally [20] the low-density linear blue shift of the Hg absorption band in the presence of He was attributed to dispersion forces. It was then necessary to assume that these were higher for Hg in the ground state than in the excited state. However these assumptions now appear to be at variance with the calculations of Margenau [21] on the effect of such dispersion forces with Hg-rare gas interactions. More recently still, blue shifts have been reported for the same transition of Hg in rare gas matrices of A, Kr and Be at 4·2°K, and for the $^2S_{1/2} \rightarrow {}^2P_{1/2,\,3/2}$ transitions of Na in an argon matrix at the same low temperature [22]. It is possible to provide an interpretation of these effects in terms of our dielectric effect, for the blue shifts due to the dielectric effect are usually superimposed on relatively large red shifts due to dispersion forces. We should therefore expect a net blue shift to be manifested in media of low polarizability,

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† The calculations of ΔE_v in table 3 were made using Buckingham's expression [16] for the dispersion force. Alternative approximations, or—in this simple case—the use of exact polarizabilities, could introduce factors of the order of 2. But such factors are irrelevant for our present purposes.

and in transitions of low oscillator strength, when the effect of dispersion forces is relatively small. The latest experimental evidence is in agreement with this view. But of course it cannot yet be said to confirm in it detail.

9. Conclusions

We have given evidence in the preceding paragraphs to support the view that the energies of the ground and excited states of an atom are affected by the presence of a surrounding medium by virtue of three quite distinct factors. These are dispersion, overlap repulsion and medium polarization effects. So also is the charge density at the nucleus of the trapped atom. Simple calculations showed that in many cases the dielectric-medium contributions were of the same order of magnitude as the others, and ought not therefore to be excluded. These calculations were simple ones, involving merely a single hydrogen atom, but there is no reason to suppose that the situation would be very different if larger atoms and molecules, for which we have only much less accurate wave functions, were used instead. It is our opinion that these present calculations have shown the importance of the dielectric effect, and represent about as far as it is worth proceeding with such very general analysis. What is now needed is a more careful study of a limited number of particular cases, in which considerable effort would be available to improve substantially on the approximate treatments used in this paper. Only then would it become possible to state with certainty what is the relative importance of our three factors. Finally, we have neglected all exchange and charge-transfer effects. These may be important at small distances, but will be expected to be small at large ones. With molecules there will also be quadrupole forces, as is shown by the pressure-induced transitions of gaseous hydrogen.

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