Dielectric medium effects on loosely bound electrons†

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The problem of electron binding in solutions is treated on the basis of a continuum model. The polarizable medium is represented by a continuum, which can be characterized by macroscopic properties, e.g. the static and the optical dielectric constants. The motion of an additive electron is determined by its interaction with the polarization produced by the electron itself. An attempt is made to treat the whole system (dielectric medium and additive electron) by employing two different approximations.

After the separation of the electronic and nuclear motion, an adiabatic separation of the motion of the medium electrons and the additive electron is carried out. An alternative approach involves the application of the Hartree–Fock self-consistent-field treatment.

A comparison of these treatments is presented.

It appears that the independent particle approximation is adequate for the treatment of electron binding in solutions.

The adequacy and scope of the continuum approximation are discussed.

1. INTRODUCTION

In recent years electronic processes in solutions have been a subject of considerable interest. These investigations include the study of electron binding in metal solutions [1, 2], electronic excitation of solvated ions [3], photochemical processes in rigid glasses [5] and in solutions [4, 6] and primary processes in the radiation chemistry of aqueous solutions [7]. The purpose of the present work is the investigation of electron binding in solutions on the basis of a continuum model. This treatment may be suitable for a physical system where the penetration of the charge distribution of the additive electron into the medium is sufficient to justify the application of the bulk properties of the medium. According to the continuum model the additional electron is affected by the polarization field of the dielectric medium. In this treatment the interaction energy is determined by long range interactions.

Previous treatments of electron binding in solutions [2, 3] were based on models previously developed for ionic crystals. These models [8–13] involve the application of the classical electrostatic picture for the computation of the energy levels of the additive electrons. Landau introduced the basic concept of the model of an additive electron bound in a dielectric medium by polarization of this medium by the electron itself ("an electron trapped by digging its own hole"). It was assumed that the permanent polarization of the medium forms the field acting on the additive electron, while the electronic polarization of the medium merely yields a shielding effect.

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In the present treatment the equations of motion of the additive electron are treated considering the whole system consisting of the dielectric medium and the additive electron. Two basic approximations are applied for the electronic wave function of the system : an adiabatic separation of the motion of the additive electron and the medium electrons, and alternatively a one-electron approximation. The polarization energy of the medium is computed by application of classical electrostatic expressions involving bulk properties, e.g. the static and optical dielectric constants. This treatment reduces the complicated n-electron problem to a one-electron treatment.

2. Electrostatic energy of a polarized dielectric

In the present treatment the electrostatic energies of both equilibrium and non-equilibrium states have to be considered. In non-equilibrium states the polarization of the medium is not determined by the charge distribution and electrical field strength in the ordinary way. The general expressions for the charging energy of a dielectric medium were recently considered by Marcus [14] and will be applied in a somewhat modified way.

Generally speaking, the polarization of a dielectric medium consists of electronic, atomic, and orientational contributions. We distinguish between the electronic component of the polarization $\mathbf{P}_e$ due to the distortion of the electronic shells of the medium molecules, and the atomic and orientational components which give rise to the 'permanent' polarization $\mathbf{P}_D$. The total polarization is the vector sum

$$\mathbf{P}=\mathbf{P}_e+\mathbf{P}_D. \tag{1}$$

An equilibrium state of the system is uniquely defined by the electric field vector $\mathbf{E}$ (determined by the electrostatic potential) and by the displacement vector $\mathbf{E}_c$ (determined by the charge distribution ρ). The polarization is a function of the field and in the absence of dielectric saturation

$$\mathbf{P}=\alpha\mathbf{E}, \tag{2}$$

where α is the polarizability of the medium. Denoting by α_e and α_D the electronic and permanent polarizabilities, then for an equilibrium state

$$\mathbf{P}_e=\alpha_e\mathbf{E}, \tag{3 a}$$

$$\mathbf{P}_D=\alpha_D\mathbf{E}, \tag{3 b}$$

where the polarizabilities can be expressed by

$$\alpha_e=\frac{D_{\mathrm{op}}-1}{4\pi}, \tag{4 a}$$

$$\alpha_D=\frac{D_{\mathrm{s}}-D_{\mathrm{op}}}{4\pi}, \tag{4 b}$$

where D_{s} and D_{op} are the static and the optical dielectric constants of the medium.

The general expression for the charging energy of a dielectric medium in equilibrium is

$$W=\frac{1}{8\pi}\int \mathbf{E}\,\mathbf{E}_c\,dv=\frac{1}{8\pi D_{\mathrm{s}}}\int \mathbf{E}_c^2\,dv. \tag{5}$$

This expression is subjected to the conditions

$$\frac{\delta W}{\delta P_e}=0, \quad \frac{\delta W}{\delta P_D}=0, \tag{6}$$

the variations being performed under conditions of fixed charge distribution.

A non-equilibrium state is specified by the polarization $\mathbf{P}$, the field strength $\mathbf{E}$, and the field strength $\mathbf{E}_c$ produced in vacuum ($D_{\mathrm{S}}=D_{\mathrm{op}}=1$) by the same charge distribution

$$\operatorname{div} \mathbf{E}_c=4\pi\rho. \tag{7}$$

For a non-equilibrium state where the electronic polarization is in equilibrium with the field and thus given by (3 *a*), while the permanent polarization attains an arbitrary value $\mathbf{P}_D$, the electrostatic charging energy is expressed by [14]

$$W'=\frac{1}{8\pi}\int \mathbf{E}_c{}^2\,dv-\frac{1}{2}\int\left[\mathbf{P}\mathbf{E}_c+\mathbf{P}_D\left(\frac{\mathbf{P}_D}{\alpha_D}-\mathbf{E}\right)\right]dv, \tag{8}$$

subjected to the condition

$$\frac{\delta W'}{\delta \mathbf{P}_e}=0. \tag{9}$$

The polarization energy of the dielectric medium U is readily obtained by subtracting from W the charging energy of the system in the same charge distribution in vacuum, which is given by

$$\frac{1}{8\pi}\int \mathbf{E}_c{}^2\,dv.$$

Hence

$$U=-\frac{1}{8\pi}\left(1-\frac{1}{D_{\mathrm{S}}}\right)\int \mathbf{E}_c{}^2\,dv \quad \text{for an equilibrium state,} \tag{10}$$

$$U'=-\frac{1}{2}\int\left[\mathbf{P}\mathbf{E}_c+\mathbf{P}_D\left(\frac{\mathbf{P}_D}{\alpha_D}-\mathbf{E}\right)\right]dv \quad \text{for a non-equilibrium state.} \tag{11}$$

Equation (11) can be transformed to an equivalent form by using the relations :

$$\mathbf{E}=\frac{\mathbf{E}_c-4\pi\mathbf{P}_D}{D_{\mathrm{op}}}, \tag{12}$$

$$\mathbf{P}_e=\frac{1}{4\pi}\left(1-\frac{1}{D_{\mathrm{op}}}\right)\mathbf{E}_c-\left(1-\frac{1}{D_{\mathrm{op}}}\right)\mathbf{P}_D, \tag{13}$$

thus leading to

$$U'=-\frac{1}{8\pi}\left(1-\frac{1}{D_{\mathrm{op}}}\right)\int \mathbf{E}_c{}^2\,dv-\frac{1}{D_{\mathrm{op}}}\int \mathbf{P}_D\,\mathbf{E}_c\,dv+\frac{2\pi D_{\mathrm{S}}}{D_{\mathrm{op}}(D_{\mathrm{S}}-D_{\mathrm{op}})}\int \mathbf{P}_D{}^2\,dv. \tag{14}$$

Another expression required for the treatment of vertical excited states is the energy change χ involved in a transformation of a system which is in equilibrium with a charge distribution ρ to a non-equilibrium state where the permanent polarization is in equilibrium with another charge distribution ρ^0. It can be shown that

$$\chi=\frac{1}{8\pi}\left(\frac{1}{D_{\mathrm{op}}}-\frac{1}{D_{\mathrm{S}}}\right)\int(\mathbf{E}_c-\mathbf{E}_c{}^0)^2\,dv, \tag{15}$$

where

$$\operatorname{div} \mathbf{E}_c=4\pi\rho \quad \text{and} \quad \operatorname{div} \mathbf{E}_c{}^0=4\pi\rho^0.$$

3. THE HAMILTONIAN AND THE ELECTRONIC WAVE FUNCTION

We consider the general system consisting of the dielectric medium, a fixed additional charge z (or generally positive charge distribution ρ_z), and the additive electron. The general form of the Hamiltonian for this system will be given by

$$\mathscr{H}=T_n+h+T_e+v_{ze}+\sum_i v_{zi}+\sum_n v_{zn}+\sum_i v_{ei}+\sum_n v_{en}, \tag{16}$$

where T_n is the kinetic energy of the nuclei, h represents the Hamiltonian of the medium in the absence of z and of e, at fixed nuclear configuration

$$h=-\frac{1}{2}\sum_i \Delta_{ri}-\sum_{n,i}\frac{Z_n}{|r_i-r_n|}+\sum_{n<m}\frac{Z_nZ_m}{|r_n-r_m|}+\sum_{i<j}\frac{1}{|r_i-r_j|}. \tag{17}$$

r_i or r_j represent the coordinates of the medium electrons, and r_n or r_m are the coordinates of the medium nuclei of charge Z_n or Z_m.

T_e is the kinetic energy of the additive electron, the coordinates of the electron being represented by r_e

$$T_e=-\tfrac{1}{2}\Delta r_e;$$

v_{ze} represents the interaction energy between z (located at r_z) and the additive electron e

$$v_{ze}=-\frac{z}{|r_e-r_z|}$$

v_{zi} and v_{zn} represent the interaction energies between the charge z and a medium electron i, or a medium nucleus n respectively. v_{ei} and v_{en} represent the interaction energies between the additive electron and a medium electron i or a medium nucleus n; thus

$$v_{zi}=-\frac{z}{|r_z-r_i|},$$

$$v_{zn}=\frac{zZ_n}{|r_z-r_m|},$$

$$v_{ei}=\frac{1}{|r_i-r_e|},$$

$$v_{en}=-\frac{Z_n}{|r_e-r_n|}.$$

The energy of the medium is given by

$$h_m=h+\sum_i v_{zi}+\sum_n v_{zn}+\sum_i v_{ei}+\sum_n v_{en} \tag{18}$$

and consists of the self-energy and the part due to polarization.

Thus setting

$$\mathscr{H}=T_n+h_m+T_e+v_{ze}=T_n+H \tag{19}$$

the total energy E of the system will be obtained from the equation

$$\mathscr{H}\Psi=E\Psi. \tag{20}$$

The nuclear motion is separated by application of the adiabatic approximation [15, 16]. The eigenfunction Ψ can be represented in the form

$$\Psi(r_i,r_e,r_n)=\varphi_{rn}(r_i,r_e)\,w(r_n). \tag{21}$$

The electronic wave function φ_{rn} depending on the nuclear coordinates as parameters is obtained from the equation

$$H\varphi_{rn}=E(r_n)\,\varphi_{r_n} \tag{22}$$

while the total energy of the system is obtained from the expression

$$(T_n + E(r_n) - E)w(r_n) = 0. \tag{23}$$

For the sake of simplicity it is convenient to consider the limiting case of infinitely heavy nuclei, when nuclear vibrations can be neglected. The total energy of the system is obtained from the condition

$$\frac{\delta E(r_n)}{\delta r_n} = 0 \quad \text{for all } r_n. \tag{24}$$

As equation (22) cannot be accurately solved approximate treatments of the electronic wave function have to be applied.

4. THE ONE-ELECTRON APPROXIMATION

A natural approach will involve the application of independent-particle theories. The electronic wave function of the system can be represented using the Hartree product

$$\varphi_{rn}(r_i, r_e) = \Phi(r_i)\psi(r_e). \tag{25}$$

The electronic energy will be represented in the form of the variation integral

$$E = \langle \Phi(r_i)\psi(r_e) \,|\, H \,|\, \Phi(r_i)\psi(r_e)\rangle. \tag{26}$$

Application of the variational theorem leads to

$$\frac{\delta E}{\delta \Phi} = 0, \tag{27 a}$$

$$\frac{\delta E}{\delta \psi} = 0, \tag{27 b}$$

subject to the auxiliary conditions

$$\langle \Phi \,|\, \Phi \rangle = 1, \tag{28 a}$$

$$\langle \psi \,|\, \psi \rangle = 1. \tag{28 b}$$

Application of equation (19) leads to the result

$$E = \langle \psi \,|\, T_e + v_{ze} \,|\, \psi \rangle + \langle \Phi \,|\, (h_m) \,|\, \Phi \rangle, \tag{29}$$

where

$$(h_m) = h + \sum_i v_{zi} + \sum_n v_{zn} + \left|\left\langle \psi \sum_i v_{ei} + \sum_n v_{en} \,|\, \psi \right\rangle\right..$$

(h_m) is determined by the *average* charge distribution of the additive electron. The second integral in equation (29) can be represented as the sum of the self-energy, μ_0, of the medium and the polarization energy U :

$$\langle \Phi \,|\, (h_m) \,|\, \Phi \rangle = \mu_0 + U(P_e, P_D, (E_c)). \tag{30}$$

Essentially the same result can be obtained by the application of the Hartree–Fock procedure. Considering the W.F. of the s medium electrons and the additional electron

$$\varphi_{rn}(r_1, \ldots, r_s, r_e) = [(s+1)!]^{-1/2} \sum_P (-1)^p P\phi_1(1)\phi_2(2)\ldots\phi_s(s)\phi_{s+1}(s+1), \tag{25'}$$

where

$$\langle \phi_i \,|\, \phi_j \rangle = \delta_{ij}, \quad i,j = 1 \ldots (s+1). \tag{28'}$$

The energy of the system is then given by

$$E=\sum_{i=1}^{s+1}\langle\phi_i|g_i|\phi_i\rangle+\sum_{i<j=1}^{s+1}\left\langle\phi_i\phi_j\left|\frac{1}{|r_i-r_j|}\right|\phi_i\phi_j\right\rangle-\left\langle\phi_i\phi_j\left|\frac{1}{|r_i-r_j|}\right|\phi_j\phi_i\right\rangle, \qquad (26')$$

where $g_i\,(i=1\ldots s+1)$ are the one-electron operators for the medium electrons and for the additive electron. It is assumed that the s spin orbitals of the medium electrons $\phi(i=1\ldots s)$ are represented by the appropriate self-consistent field wave functions. By setting $\psi=\phi_{s+1}$ the energy is presented in the form

$$\begin{aligned}E=&\langle\psi\,|\,T_e+v_{ze}\,|\psi\rangle+\sum_{i=1}^{s}\langle\phi_i|g_i|\phi_i\rangle\\&+\sum_{i<j=1}^{s}\left\langle\phi_i\phi_j\left|\frac{1}{|r_i-r_j|}\right|\phi_i\phi_j\right\rangle-\left\langle\phi_i\phi_j\left|\frac{1}{|r_i-r_j|}\right|\phi_j\phi_i\right\rangle\\&+\sum_{i=1}^{s}\left\langle\phi_i\psi\left|\frac{1}{|r_i-r_e|}\right|\phi_i\psi\right\rangle-\left\langle\phi_i\psi\left|\frac{1}{|r_i-r_e|}\right|\psi\phi_i\right\rangle.\end{aligned} \qquad (26'')$$

Equation (26″) is subjected to the extremum conditions $\delta E/\delta\phi_i=0$ for $i=1\ldots s+1$ with the auxiliary conditions (28′). Substitution of the unperturbed spin orbitals of the medium electrons into (26″) leads to the expression

$$E=\langle\psi\,|\,T_e+v_{ze}\,|\psi\rangle+\mu_0+U(\mathbf{P}_e,\mathbf{P}_D,(\mathbf{E}_c)). \qquad (29')$$

$U(\mathbf{P}_e,\mathbf{P}_D,(\mathbf{E}_c))$ represents the polarization energy of the dielectric medium by the fixed charge Z and by the mean charge distribution, $|\psi|^2$, of the additive electron:

$$(\mathbf{E}_c)=(\mathbf{E}_e)+\mathbf{E}_z, \qquad (31)$$

where the electronic contribution is defined by

$$\left.\begin{aligned}\operatorname{div}(\mathbf{E}_e)&=-4\pi|\psi|^2,\\(\mathbf{E}_e)&=-\operatorname{grad}f,\\\Delta f&=4\pi|\psi|^2.\end{aligned}\right\} \qquad (32)$$

f is the electrostatic potential due to the charge distribution $-|\psi|^2$, $\mathbf{E}_z$ is the contribution of the fixed charge distribution, and can be represented by

$$\mathbf{E}_z=-\operatorname{grad}v_{ze}. \qquad (33)$$

Since E is subject to the minimum conditions (27 *a*) and (24), applying the macroscopic properties of the dielectric medium we have

$$\frac{\delta U}{\delta P_e}=0,\quad\frac{\delta U}{\delta P_D}=0. \qquad (34)$$

Hence the polarization energy of the medium is represented by the equilibrium value (equation (10)).

Substitution of (31) in equation (10) leads to

$$E=\langle\psi|T_e+v_{ze}|\psi\rangle-\frac{1}{8\pi}\left(1-\frac{1}{D_s}\right)\int(\mathbf{E}_c)^2\,dv+\mu_0, \qquad (35)$$

$$E=\langle\psi|T_e+v_{ze}|\psi\rangle-\frac{1}{8\pi}\left(1-\frac{1}{D_s}\right)\int[(\mathbf{E}_e)^2+2(\mathbf{E}_e)\mathbf{E}_z+\mathbf{E}_z{}^2]\,dv+\mu_0. \qquad (36)$$

The integrals appearing in (36) can be transformed by application of Green's theorem and equations (32) and (33). Hence

$$\int(\mathbf{E}_e)\mathbf{E}_z\,dv=4\pi\langle\psi|v_{ze}|\psi\rangle \qquad (37)$$

and

$$\int (\mathbf{E}_e)^2\,dv = -4\pi\langle\psi|f|\psi\rangle. \tag{38}$$

Substitution in equation (36) leads to

$$\left\langle\psi\left|T_e+\frac{1}{D_{\mathrm{S}}}v_{ze}+\frac{1}{2}\left(1-\frac{1}{D_{\mathrm{S}}}\right)f\right|\psi\right\rangle-\frac{1}{8\pi}\left(1-\frac{1}{D_{\mathrm{S}}}\right)\int \mathbf{E}_z{}^2\,dv+\mu_0. \tag{39}$$

The second integral in equation (39) represents the polarization energy of the medium by the additive fixed charge z. By choosing a reference state which corresponds to the self-energy of the medium polarized by the fixed charge z the energy is

$$E=\left\langle\psi\left|T_e+\frac{1}{D_{\mathrm{S}}}v_{ze}+\frac{1}{2}\left(1-\frac{1}{D_{\mathrm{S}}}\right)f\right|\psi\right\rangle. \tag{40}$$

Application of the variational treatment (equations (27*b*) and (28*b*)) readily leads to

$$\left\langle\delta\psi\left|T_e+\frac{1}{D_{\mathrm{S}}}v_{ze}+\left(1-\frac{1}{D_{\mathrm{S}}}\right)f\right|\psi\right\rangle=0, \tag{41}$$

and

$$\langle\delta\psi|\psi\rangle=0.$$

Hence the wave function of the additive electron can be obtained from the equation

$$\left[T_e+\frac{1}{D_{\mathrm{S}}}v_{ze}+\left(1-\frac{1}{D_{\mathrm{S}}}\right)f\right]\psi=\epsilon\psi \tag{42}$$

with

$$\Delta f=4\pi|\psi|^2.$$

This equation is not a usual eigenvalue problem as the potential energy depends on the wave function of the electron itself. This integro-differential equation can be solved by the self-consistent variation method as suggested by Mott and Gurney [10]. Alternatively, the total energy of the system may be obtained from equations (40) and (41).

From equations (40) and (42) we calculate the polarization energy of the medium required for the formation of the potential well in which the additional electron is bound:

$$\pi=\epsilon-E=\frac{1}{2}\left(1-\frac{1}{D_{\mathrm{S}}}\right)\langle\psi|f|\psi\rangle. \tag{43}$$

5. THE ADIABATIC APPROXIMATION

An approximate solution for the electronic wave function can be obtained by assuming that the average velocity of the additional, loosely bound, electron is small compared with those of the core and valence electrons of the medium particles. The binding energy, and thus by the virial theorem the average kinetic energy of the additive electron, is relatively low. Tentatively an approximation is applied which is equivalent to the adiabatic approximation in molecular physics. The additive electron is considered to be temporarily at rest at some position r_e. The medium electrons are affected by a potential of a fixed point charge at r_e. On the other hand, the loosely bound electron 'sees' a potential due to the average distribution of the medium electrons. This method is similar to Bethe's treatment of the excited states of He [17].

This discrimination between the tightly bound medium electrons and the loosely bound additive electron can be formulated in the form

$$\varphi_{rn}(r_i, r_e)=\phi(r_i;\, r_e)\psi(r_e). \tag{44}$$

$\phi(r_i;\, r_e)$ is the wave function of the medium electrons and depends parametrically on r_e. $\psi(r_e)$ represents the wave function of the additive electron.

Following the general approach of the adiabatic approximation [15, 16] the wave function ϕ for the medium electrons is obtained from

$$h_m\phi(r_i;\, r_e)=e(r_e,\, r_n)\phi(r_i;\, r_e). \tag{45}$$

This equation describes the states of the medium electrons for fixed r_e and all r_n. The total energy of fixed nuclear configuration will be obtained from

$$[T_e+v_{ze}+e(r_e,\, r_n)]\psi=E(r_n)\psi \tag{46}$$

and the application of the conditions (24) to $E(r_n)$ leads to the total energy of the system.

Equation (45) can be treated by application of the variation–perturbation treatment [17]. Consider the eigenvalue problem (45)

$$(h+\lambda h'-e)\phi=0, \tag{47}$$

where

$$\lambda h'=h_m-h. \tag{48}$$

The eigenfunctions and eigenvalues are expanded in terms of

$$e=\sum_{n=0}^{\infty}\lambda^n e_n;\quad \phi=\sum_{n=0}^{\infty}\lambda^n\phi_n, \tag{49}$$

whence

$$h\phi_n+h'\phi_{n-1}-\sum_{m=0}^{n}e_m\phi_{n-m}=0 \text{ for all } n \tag{50}$$

leading to

$$e=\langle\phi_0|h|\phi_0\rangle+\langle\phi_0|h'|\phi_0\rangle+\langle\phi_0|h'|\phi_1\rangle+\dots, \tag{51}$$

thus $\mu_0=\langle\phi_0|h|\phi_0\rangle$ represents the self-energy of the unpolarized medium, while

$$U=\langle\phi_0|h'|\phi_0\rangle+\langle\phi_0|h'|\phi_1\rangle+\dots$$

represents the polarization energy of the dielectric medium.

Thus we set

$$e=\langle\phi|h_m|\phi\rangle=\mu_0+U(\mathbf{P}_e,\, \mathbf{P}_D,\, \mathbf{E}_c); \tag{52}$$

e is obtained from

$$\frac{\delta e}{\delta\phi}=0;\quad \langle\phi|\phi\rangle=1; \tag{53}$$

E_c is the field produced in vacuum by the point sources at r_e and r_z:

$$\mathbf{E}_c=\mathbf{E}_e+\mathbf{E}_z, \tag{54}$$

where $\mathbf{E}_z$ is given by (33) and

$$\operatorname{div}\mathbf{E}_e(r)=-4\pi\delta(r-r_e), \tag{55}$$

where δ is Dirac's delta function.

The variation problem (53) is equivalent to the condition $\delta U/\delta P_e=0$. Thus we have to consider the polarization energy of the medium for the case when the electronic polarization *only* has attained its equilibrium value. Equation (46) will be solved by the variation method

$$E(r_n)=\langle\psi|T_e+v_{ze}+U|\psi\rangle+\mu_0, \tag{56}$$

where U is now given by equation (14). Substitution of equations (14) and (54) in (56) leads to the result

$$E(r_n)=\langle\psi|T_e+v_{ze}|\psi\rangle-\frac{1}{8\pi}\left(1-\frac{1}{D_{\mathrm{op}}}\right)\int\langle\psi|\mathbf{E}_e^2+2\mathbf{E}_e\mathbf{E}_z+\mathbf{E}_z^2|\psi\rangle\,dv$$
$$-\frac{1}{D_{\mathrm{op}}}\int\langle\psi|\mathbf{P}_D[\mathbf{E}_e+\mathbf{E}_z]|\psi\rangle\,dv+\frac{2\pi D_{\mathrm{S}}}{D_{\mathrm{op}}(D_{\mathrm{S}}-D_{\mathrm{op}})}\int\mathbf{P}_D^2\,dv+\mu_0. \qquad (57)$$

Application of equations (55), (33) and Green's theorem leads to

$$\int\langle\psi|\mathbf{E}_e\mathbf{E}_z|\psi\rangle\,dv=4\pi\langle\psi|v_{ze}|\psi\rangle, \qquad (58)$$

while using the definition (32) and equation (55) we get

$$\int\langle\psi|\mathbf{P}_D\mathbf{E}_e|\psi\rangle\,dv=\int\mathbf{P}_D(\mathbf{E}_e)\,dv. \qquad (59)$$

The energy integral is given in the form

$$E(r_n)=\left\langle\psi\middle|T_e+\frac{1}{D_{\mathrm{op}}}v_{ze}\middle|\psi\right\rangle-\frac{1}{8\pi}\left(1-\frac{1}{D_{\mathrm{op}}}\right)\int\mathbf{E}_e^2\,dv$$
$$-\frac{1}{D_{\mathrm{op}}}\int\mathbf{P}_D[\mathbf{E}_z+(\mathbf{E}_e)]dv+\frac{2\pi D_{\mathrm{S}}}{D_{\mathrm{op}}(D_{\mathrm{S}}-D_{\mathrm{op}})}$$
$$\times\int\mathbf{P}_D^2\,dv-\frac{1}{8\pi}\left(1-\frac{1}{D_{\mathrm{op}}}\right)\int\mathbf{E}_z^2\,dv+\mu_0. \qquad (57')$$

The integral $\int\mathbf{E}_e^2\,dv$ is infinite. This is due to the present model of a charge point source in a continuous dielectric medium. However, the value of this integral is independent of r_e and r_n. Thus as long as states within the medium are considered this integral is merely an additive constant.

The integral $E(r_n)$ is subjected to the conditions $\delta E/\delta\psi=0$ and $\delta E/\delta r_n=0$. As the order of these operations is immaterial the condition (24) will be applied first. This condition is equivalent to $\delta E/\delta P_D=0$ thus leading to

$$\mathbf{P}_D=\frac{1}{4\pi}\frac{D_{\mathrm{S}}-D_{\mathrm{op}}}{D_{\mathrm{S}}}[E_z+(\mathbf{E}_e)]. \qquad (60)$$

This result indicates that in the adiabatic approximation the permanent polarization is determined by the average distribution of the bound electron. This was the basic assumption used in previous models [8–13].

Thus the energy of the system at equilibrium nuclear configuration is given by

$$E=\left\langle\psi\middle|T_e+\frac{1}{D_{\mathrm{op}}}v_{ze}\middle|\psi\right\rangle-\frac{1}{8\pi}\left(\frac{1}{D_{\mathrm{op}}}-\frac{1}{D_{\mathrm{S}}}\right)\int[(\mathbf{E}_e)^2+2\mathbf{E}_e\mathbf{E}_z]\,dv$$
$$-\frac{1}{8\pi}\left(1-\frac{1}{D_{\mathrm{op}}}\right)\int\mathbf{E}_e^2\,dv+\mu_0. \qquad (61)$$

The reference state of the energy is chosen as corresponding to the medium polarized by the point sources z and e. Application of equations (37), (38) and (61) leads to the result

$$E=\left\langle\psi\middle|T_e+\frac{1}{D_{\mathrm{S}}}v_{ze}+\frac{1}{2}\left(\frac{1}{D_{\mathrm{op}}}-\frac{1}{D_{\mathrm{S}}}\right)f\middle|\psi\right\rangle. \qquad (62)$$

Application of the variation treatment to equation (62) finally leads to the eigenvalue problem

$$\left[T_e+\frac{1}{D_{\mathrm{S}}}v_{ze}+\left(\frac{1}{D_{\mathrm{op}}}-\frac{1}{D_{\mathrm{S}}}\right)f\right]\psi=\epsilon\psi, \tag{63}$$

where

$$\Delta f=4\pi|\psi|^2.$$

The polarization energy of the medium is in this approximation

$$\pi=\frac{1}{2}\left(\frac{1}{D_{\mathrm{op}}}-\frac{1}{D_{\mathrm{S}}}\right)\langle\psi|f|\psi\rangle. \tag{64}$$

The results of (62)–(64) are identical with the approach based on Landau's theory [8].

6. Application to excited states

The treatment of excited states in equilibrium with the nuclear configuration is almost straightforward, and the corresponding energies can be readily obtained by inserting in equations (40)–(42) or (62) and (63) the wave function ψ_i representing the excited state. A difficulty arising in relation with this treatment is due to non-spherically charge distribution in the excited state. This would lead to an angular dependence of $(E_e^i(\psi_i))$ and of $f_i(\psi_i)$ corresponding to the excited state. In the present treatment this difficulty is disregarded, and an average spherically symmetrical charge distribution in the excited state is considered. A similar averaging process is carried out in the solution of the Hartree–Fock equations for atoms [18]. The following results are obtained for excited states which are in equilibrium with the nuclear framework.

For the one electron approximation

$$\left.\begin{aligned}&E_i=\left\langle\psi_i\left|T_e+\frac{1}{D_{\mathrm{S}}}v_{ze}+\frac{1}{2}\left(1-\frac{1}{D_{\mathrm{S}}}\right)f_i\right|\psi_i\right\rangle\\ \text{and}\quad&\\ &\left[T_e+\frac{1}{D_{\mathrm{S}}}v_{ze}+\left(1-\frac{1}{D_{\mathrm{S}}}\right)f_i\right]\psi_i=\epsilon_i\psi_i;\quad \Delta f_i=4\pi|\psi_i|^2\end{aligned}\right\}. \tag{65}$$

For the adiabatic approximation the result is of the same form but $(1/D_{\mathrm{op}}-1/D_{\mathrm{S}})$ has to be substituted for $(1-1/D_{\mathrm{S}})$.

Electronic transitions are subject to the restrictions of the Franck–Condon principle. Within the limits of the semi-classical formulation [19] immediately after the electronic transition the excited state is formed in the nuclear configuration corresponding to the ground state. Thus in the vertical excited state the electronic polarization has adjusted itself to the new charge distribution $-|\psi_i|^2$, while the permanent polarization is still determined by the ground state charge distribution $-|\psi|^2$. The energy E_i^v of the vertically excited state is related to the equilibrium energy of this state by

$$E_i^v=E_i+\chi, \tag{66}$$

where χ is the energy required to transform the nuclear framework which is in equilibrium with the charge distribution $-|\psi_i|^2$ into the nuclear configuration which is determined by $-|\psi|^2$. Application of equation (15) leads to

$$\chi=\frac{1}{8\pi}\left(\frac{1}{D_{\mathrm{op}}}-\frac{1}{D_{\mathrm{S}}}\right)\int[(\mathbf{E}_e^i)-(\mathbf{E}_e)]^2\,dv, \tag{67}$$

where $(\mathbf{E}_e)$ is given by equation (32) and

$$\left.\begin{aligned} \operatorname{div}(\mathbf{E}_e{}^i) &= -4\pi|\psi_i|^2, \\ (\mathbf{E}_e{}^i) &= -\operatorname{grad} f_i, \\ \Delta f_i &= 4\pi|\psi_i|^2. \end{aligned}\right\} \tag{68}$$

As χ is a positive definite quantity the energy of the vertically excited state is higher than the corresponding equilibrium state. The energy of the additive electron in the vertically excited state is obtained from

$$\frac{\delta E_i{}^v}{\delta\psi_i} = 0, \quad \langle\psi_i|\psi_i\rangle = 1. \tag{69}$$

For the one-electron approximation the following result is obtained for the vertical state resulting from the transition:

$$\begin{aligned} E_i{}^v = \left\langle\psi_i\left| T_e + \frac{1}{D_\mathrm{s}} v_{ze} + \frac{1}{2}\left(1 - \frac{1}{D_\mathrm{op}}\right) f_i + \left(\frac{1}{D_\mathrm{op}} - \frac{1}{D_\mathrm{s}}\right) f \right|\psi_i\right\rangle \\ - \frac{1}{2}\left(\frac{1}{D_\mathrm{op}} - \frac{1}{D_\mathrm{s}}\right)\langle\psi|f|\psi\rangle. \end{aligned} \tag{70}$$

Application of (69) leads to

$$\left[T_e + \frac{1}{D_\mathrm{s}} v_{ze} + \left(1 - \frac{1}{D_\mathrm{op}}\right) f_i + \left(\frac{1}{D_\mathrm{op}} - \frac{1}{D_\mathrm{s}}\right) f\right]\psi_i = \epsilon_i{}^v\psi_i, \tag{71}$$

and

$$\Delta f_i = 4\pi|\psi_i|^2.$$

Application of the adiabatic approximation readily yields the following results for the total energy:

$$E_i{}^v = \left\langle\psi_i\left| T_e + \frac{1}{D_\mathrm{s}} v_{ze} + \left(\frac{1}{D_\mathrm{op}} - \frac{1}{D_\mathrm{s}}\right) f \right|\psi_i\right\rangle - \frac{1}{2}\left(\frac{1}{D_\mathrm{s}} - \frac{1}{D_\mathrm{op}}\right)\langle\psi|f|\psi\rangle \tag{72}$$

and for the wave equation of the additive electron

$$\left[T_e + \frac{1}{D_\mathrm{s}} v_{ze} + \left(\frac{1}{D_\mathrm{op}} - \frac{1}{D_\mathrm{s}}\right) f\right]\psi_i = \epsilon_i{}^v\psi_i. \tag{73}$$

These results imply that within the limits of the adiabatic approximation the energy of the additive electron in the vertically excited state is independent of the charge distribution in this state. Thus equation (73) is an ordinarily eigenvalue problem. On the other hand the application of the one-electron approximation leads to equation (71) which is a self-consistent field problem.

7. DISCUSSION

The continuum models previously applied to problems of electron binding in liquids and solids [2, 8–12] were based on the electronic adiabatic approximation. A recent treatment of environmental effects on Rydberg transitions [20, 21] was however based on the one-electron approximation. These treatments were essentially based on semi-classical electrostatic considerations. It is desirable to consider the scope of applicability of these treatments.

A general formulation of the adiabatic approximation in molecular physics [16] may be readily applied to the adiabatic separation of the motion of the additive electron.

Let $\Phi^N(r_i;\, r_e)$ be a solution of equation (45). The actual wave equation is given from (22)

$$[H-E(r_n)]\varphi=0. \tag{22'}$$

φ is expanded in the form

$$\varphi(r_i, r_e)=\sum_N \psi^N(r_e)\Phi^N(r_i;r_e). \tag{74}$$

This expansion should contain the contribution of the continuum states. By substitution of (74) in (22′), multiplying by $\Phi^{N*}(r_i;\, r_e)$, integrating over all $d\tau_i(i=1\ldots s)$ and setting $T_e=p_e^2/2m$, the following result is obtained:

$$[T_e+e^N(r_e)-E(r_n)]\psi^N+\sum_{N'} C_{NN'}\psi^{N'}=0, \tag{75}$$

where

$$C_{NN'}=\frac{1}{m}\left(\langle\phi^N|p_e|\phi^{N'}\rangle p_e+\tfrac{1}{2}\langle\phi^N\,|\,p_e^2|\phi^{N'}\rangle\right). \tag{76}$$

For a stationary state ϕ^N may be chosen as real, then

$$C_{NN}=\langle\phi^N|T_e|\phi^N\rangle$$

and the eigenvalue problem is

$$(T_e+e^N+\langle\phi^N|T_e|\phi^N\rangle-E(r_n))\psi^N+\sum_{N\neq N} C_{NN'}\psi^{N'}=0. \tag{75'}$$

A certain justification for neglecting C_{NN} in the present treatment can be obtained by considering equation (49):

$$\phi^N(r_i;\, r_e)=\phi_0{}^N(r_i)+\phi_1{}^N(r_i;\, r_e)+\ldots\ . \tag{49'}$$

Only a small part of $\phi^N(r_i;\, r_e)$ is dependent on r_e. This correction term involves the polarization effect of the additive electron on the medium electrons.

Thus $C_{NN}=\langle\phi_0{}^N+\phi_1{}^N|T_e|\phi_1{}^N\rangle$ which may be small almost everywhere.

In this treatment the coupling parameters $C_{NN'}(N\neq N')$ are neglected. Application of perturbation theory indicates that their influence may be negligible if the electronic ground state of the medium is separated from all other states by a large gap. These arguments will probably be completely wrong when r_e is located within the core of the medium molecules. In this case the coefficients $C_{NN'}$ (all N') cannot be neglected.

The physical basis of the electronic adiabatic separation suggests that this approach will be adequate when the frequencies of the motion of the medium electrons are much higher than the frequency of the additive electron. Thus the condition required is $e^N-e^0\gg\epsilon$, where e^N is given by (45), e^0 is the ground state electronic energy of the medium, and ϵ the self-energy of the additive electron is given by equation (63). For polar liquids (e.g. liquid ammonia) ϵ calculated on the basis of the adiabatic approximation is of the order of 1–2 ev. For liquid ammonia the excitation energy of the solvent molecule is of the order of 5 ev and the ionization energy 10 ev. Thus it appears that the application of the adiabatic approximation to problems of electron binding in polar liquids is not *a priori* justified. On the other hand the binding energies of an additive electron in polar crystals is much lower, being of the order of $E=0{\cdot}13$ ev in NaCl [22]. In this case the application of the adiabatic approximation has a more sound physical basis. Another difficulty involved in the present formulation of the electronic adiabatic approximation is the neglect of exchange. This effect will be again of importance in the vicinity of the cores of the medium particles. This omission of exchange may give rise to too extended charge distribution of the additive electron.

The one-electron approximation is based on the picture of every electron moving in the average field of other electrons. This assumption is certainly adequate for the trapped electron, but in certain cases may be inadequate for the core electrons. The correlation term is not properly accounted for in this approach.

The one-electron approximation is free from this difficulty of the existence of a constant divergent integral obtained by the electronic adiabatic treatment. It thus appears that the adiabatic approximation will be inadequate for the treatment of the photoelectric effect. This difficulty could however be removed by applying a hole model which implies electron binding in a trapping centre consisting of a spherical cavity in the dielectric medium.

According to the continuous dielectric models the major difference between the adiabatic and one-electron approximations is due to the different treatment of the electronic polarization in these two cases. This is reflected in the results obtained for vertically excited states. In the one-electron approximation the nature of the many-body problem is also reflected in the wave equation for the excited state which is a self-consistent problem. In the adiabatic approximation the excited state energy is determined only by the ground state charge distribution.

Another interesting point involves the usual separation of electronic and nuclear motion. In the present treatment the static approximation [23] was employed, and the interaction between nuclear and electronic motion was neglected. For extremely loosely bound electrons in crystals the application of the Born–Oppenheimer approximation is open to criticism. However, for electrons bound in polar solvents the binding energy of the additional electron is sufficient to make the static approximation applicable.

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