

THE REPULSION POTENTIAL OF UNOCCUPIED STATES

Потенциал отталкивания незаполненных состояний

Hellmann [1] showed that the orthogonalization of the wave functions of the valency electrons on the wave functions of the electrons of the closed shells of ions can be replaced to a certain approximation by the so-called repulsion potential. The advantage of this formulation lies in the fact that the wave functions of the valency electrons, which are the solution of the Schrödinger equation with a Hamiltonian extended by the repulsion potential, do not have to be orthogonalized to wave functions of the electrons of an ion. The Hellmann conception was elaborated in detail by Gombás, who, apart from Hellmann's semi-empirical expression, also derived for the repulsion potential a number of other expressions based on the statistic formulation of the Pauli principle [2, 3, 4]. All these expressions, the wave mechanical interpretation of which was given by Fényés [5] and Szépfalusy [6], were successfully used for solving a number of problems the exact formulation of which would otherwise have been extremely complicated.

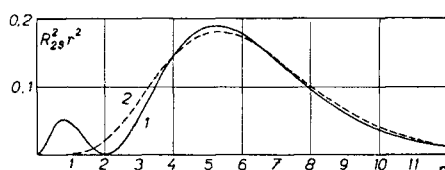


Fig. 1. 1 — exact wave function, 2 — approximative wave function.

The repulsion potential has only been used up to now on the assumption that all shells of the ion are fully occupied. When solving some problems, however, this condition is not fulfilled and the use of the repulsion potential, which was derived on this condition, is problematic.

In order to obtain an idea of the advantages of using the repulsion potential even when some states of the ion are not occupied, we considered the simple case when the approximate solution of the Schrödinger equation can be compared with the exact solution and calculated some excited states of a hydrogen atom. It is obvious that in this case we are concerned with the formal use of the repulsion potential which follows from the fact that wave functions of lower unoccupied states to which the corresponding excited state of the electron is orthogonal, are used in constructing the repulsion potential. During actual calculations use was made of the commonest expression for the repulsion potential

$$G_l = - \frac{\pi^2}{8(2l+1)} e a_0 D_l^2 - \frac{1}{4} e a_0 \frac{1}{r^2},$$

where $-e$ is the elementary charge of the electron, a_0 the radius of the lowest orbit in the hydrogen atom and D_l the fictive radial density of all unoccupied states with an azimuthal quantum number l , the energy of which is lower than the energy of the state considered. The wave function of the electron in the excited state was assumed to be of the form

$$\psi = \text{const } r^k e^{-\lambda r} \tag{1}$$

and the corresponding energy was calculated as a function of the values of the parameters k and λ , where for the sake of simplicity k takes only integral values. The minima of energy for the states $2s, 3s, 3p, 4s, 4p$ and $4d$ were determined from the course of this dependence. The values of λ determined in this way (in units of $1/a_0$), k and the energy E (in Ry) are given in Tab. 1 together with the known exact values of the energy E_{exact} (in Ry). For illustrative purposes Fig. 1 shows the exact and approximative wave function of the state $2s$. From a comparison of the values in Tab. 1 it follows that with growing principal quantum number the percentage error in the energy of the individual states s, p, d (expressed in the last column in tab. 1) increases. At the same time the approximation of the correct wave function by function (1) is worse.

In order to obtain an idea of the magnitude of the contribution of the individual energies in this formulation, we compare for example those for the state $2s$ with the exact values. From our calculations we obtain for the potential energy the value -0.377 Ry, while the exact value is -0.5 Ry. Similarly the sum of the kinetic energy 0.064 Ry and the energy

Table 1

	E_{exakt}	E	k	λ	Errors in %
2s	-0.25	-0.252	2	0.565	1
3s	-0.111	-0.120	4	0.42	8
3p	-0.111	-0.122	4	0.48	10
4s	-0.0625	-0.075	4	0.23	20
4p	-0.0625	-0.072	4	0.23	15
4d	-0.0625	-0.068	5	0.315	9

corresponding to the repulsion potential 0.061 Ry, which is 0.125 Ry, is half that of the exact value 0.25 Ry. It is thus obvious that although both the wave function and the value of the total energy in this approximation are in fairly good agreement with the exact solution of the state 2s, there are considerable differences between the corresponding energies. This is quite analogous with the other states considered.

This fact somewhat explains the validity of the assumptions made in papers [5], [6], according to which in the first approximation the mean values of all the energies, with the exception of the radial part of the kinetic energy, are approximately equal to values of the exact solution. It is obvious from our calculations that even when this assumption is not fulfilled the approximation of the wave function and the corresponding value of the total energy can be in good agreement with the exact solutions in spite of the fact that during interpretation of the values of the individual energies great care must be taken with respect to the certain mutual compensation.

In conclusion it can be said that the use of the repulsion potential for unoccupied states can, under certain conditions in cases where orthogonalization would lead to extremely complicated calculations, reproduce the values of the total energy and the corresponding wave function with sufficient accuracy.

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THE EFFECT OF IRRADIATION ON THE DIELECTRIC LOSSES
OF LUMINESCENT ZINC-CADMIUM SULPHIDE

Влияние облучения на диэлектрические потери люминесцентного сульфида ZnS-CdS

It is known from recent papers [1] that the dielectric losses of luminescent materials increase on irradiation. There is little information to hand, however, on the spectral dependence of this phenomenon. An experiment was therefore carried out in which zinc-cadmium sulphide (50% CdS), activated by silver, was irradiated through Schott filters using a projection bulb. The sample was placed in a condenser having one glass electrode coated with a conductive layer of tin chloride. In order to eliminate the possibility of a short circuit a polystyrene foil 10 μ thick was placed between the glass electrode and the sample. The air in the space between the electrodes was expelled by a few drops of mineral oil. The 2 mm thick filters used transmit 50% of the incident radiation at the following wavelengths