

ENERGIES AND WAVE FUNCTIONS OF THE U-2 CENTER

J. D. Patterson and R. L. Petersen
Physics Department, South Dakota School of Mines
and Technology, Rapid City

The U-2 center is an interstitial hydrogen atom in an alkali halide. It can be pictured as shown in Figure 1. In Figure 1, the distance to a nearest neighbor (positive or negative ion) is $R = \frac{\sqrt{3}}{2} a \approx 5.13$ a.u. (for KCl), where 1 a.u. is approximately .53 Å. We wish to use a one electron approximation to estimate the ground state wave function and energy of the electron trapped by the interstitial proton.

Experiments by Delbecq, Smaller and Yuster¹ have told us that (a) paramagnetic resonance (absorption width) implies that $|\psi(0)|^2 = 1/\pi = .32$ a.u., and (b) optical absorption implies that $E_{\text{first excited}} - E_{\text{ground}} = 5.25$ eV. We can use these values to help check our calculations. $\psi(0)$ is the wave function of the trapped electron at the proton. E is the energy of the trapped electron.

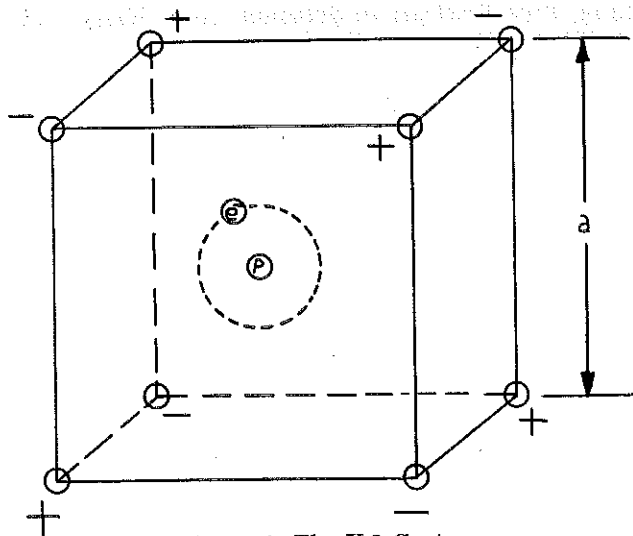


Figure 1. The U-2 Center.

There are two possible viewpoints for doing a calculation. The first viewpoint is that the very polarizable negative ions are quite

close so that one should take this into account by using a continuum model of the potential. Dielectric constants are used to describe the polarization. Of course, one will have to modify this model so as to take into account the fact that one doesn't have any shielding (and hence no dielectric constant) when the electron is near the proton. This is the viewpoint we shall adopt.

The second viewpoint is that in the ground state the hydrogen atom only has a "radius" of 1 Bohr unit. Thus hopefully, one can neglect any overlapping with the neighboring ions. Further, the potential of the positive and negative ions cancel to first order, so that in the ground state the U-2 center really is an interstitial hydrogen atom. Since in atomic units, the ground state wave function of the hydrogen atom is

$$\psi_{1s}(r) = (1/\sqrt{\pi}) \text{Exp}(-r),$$

paramagnetic resonance strongly supports this view. The idea is then that the first excited state is lowered considerably by the interactions with the surroundings, so as to give the measured energy of transition. If overlapping effects are really negligible, then a point ion model should suffice for the ground state. In fact, H. Mimura and Y. Uemura² have been successful with this model in interpreting the order of magnitude of the paramagnetic resonance results. We have not used this model, because it does not appear to give any idea of how to calculate the first excited state. Besides, we regard the statement that in the ground state the U-2 center is just like a hydrogen atom as open to question.

In our model, for large distances from the proton we have used the self consistent continuum potential of J. H. Simpson.³ For small distances we have assumed the Colombic potential $V(r) \propto - (1/r)$. In between these limits, we assume a smooth variation of the potential. We have defined a parameter R which measures the transition between these limits. Thus we have,

$$\langle \psi_{1s} | H | \psi_{1s} \rangle = \langle \psi_{\eta} | -\frac{1}{2m^*} \nabla^2 | \psi_{\eta} \rangle + \langle \psi_{\eta} | V(R, \psi_{\eta}) | \psi_{\eta} \rangle \quad (1)$$

By the variational theorem

$$\left(\frac{\partial \langle \psi_{1s} | H | \psi_{1s} \rangle}{\partial \eta} \right)_{\eta=\mu} = 0 \quad \text{where} \quad \psi_{\eta} = (1/\sqrt{\pi}) \eta^{3/2} e^{-\eta r}, \quad (2)$$

which implies that

$$\eta = \eta(m^*, R) \quad (3)$$

for an energy minimum. Thus, for the best approximation to the energy we get

$$W = W(R, m^*, \eta) = \langle \psi_{1s} | H | \psi_{1s} \rangle_{\eta=R} = W(R, m^*, \eta(R, m^*)) \quad (4)$$

If we assume $m^* \approx 1$, and $R \approx 4.6$ a.u. then our calculation says

$$\begin{aligned} \eta &\approx 1 \text{ a.u. (in agreement with paramagnetic resonance), and} \\ W &\approx -.45 \text{ a.u.} = -12.2 \text{ eV. An unperturbed hydrogen atom has an energy} \\ &\text{of } -13.6 \text{ eV.} \end{aligned}$$

These calculations are quite consistent with the idea that the hydrogen atom is almost unperturbed. A better check would be to calculate the energy of the first excited state using the same values of R (and perhaps m^*). This as yet has not been done. Note that we have approximately taken into account overlapping effects. Note also that we now have some idea for a potential for calculating the first excited state.

However, in general it is unrealistic to use the value of the wave function at one point to determine its value over all space. This process is implied when we use a one parameter wave function and

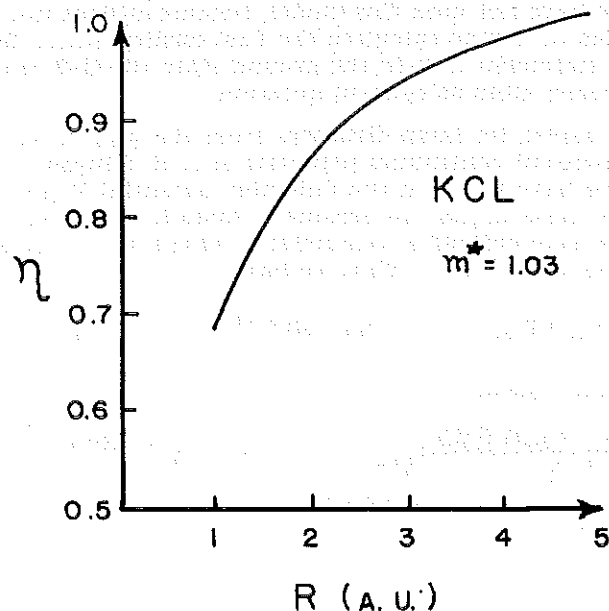


Figure 2. Variation of η with R for the ground state.

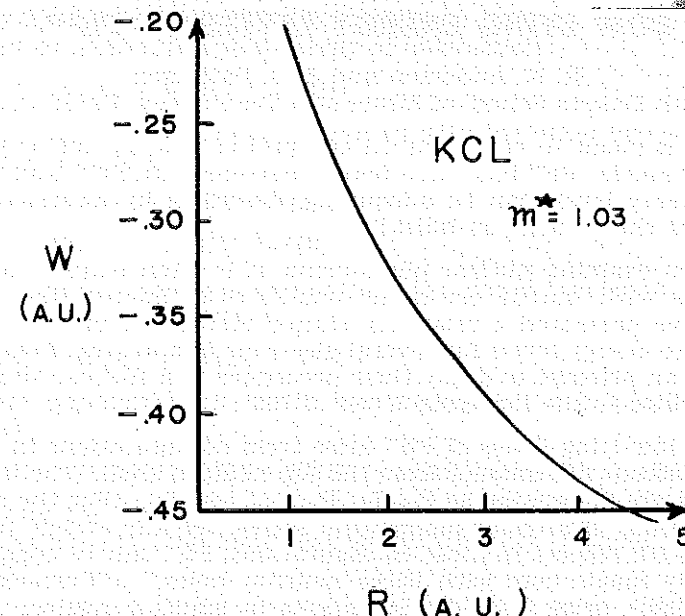


Figure 3. Variation of the ground state energy with R .

require it to fit the paramagnetic resonance data. We still believe the unperturbed nature of the hydrogen atom to be an open question. Figures 2 and 3 show the results our model yields for several values of R . The calculations were done with a FORTRAN program on an IBM 1620 Computer.

We note that for $R \approx \frac{\sqrt{3}}{2} a$, η and W are not very sensitive functions of R . This is consistent with a small hydrogen atom. It is possible that a more refined trial wave function would give paramagnetic resonance agreement without requiring an unperturbed hydrogen atom.

REFERENCES

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3. J. H. Simpson, *Proc. Roy. Soc.* **A197**, 269 (1949).