

# Schrödinger Equation: How Was it Derived and Used in VSCF and Ab Initio Projects

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## Erwin Schrödinger



Figure 1. Erwin Schrödinger (1887-1961): Nobel Prize in Physics 1933.

Erwin Schrödinger articles entitled "Quantization as Eigenvalue Problem" have been published in *Annalen der Physik* in January, 1926.

### List of scientific discoveries which facilitated obtaining of the Schrödinger equation

Erwin Schrödinger used also discoveries of other scientists in obtaining his famous equation.

- **Wave equation first derived by Jean Le Rond d'Alembert with wave phase velocity  $v_p$**
- **Max Planck formula for energy of quanta  $E = h\nu = \hbar\omega$**
- **Louis de Broglie hypothesis  $\lambda = h/p$**

where  $E$  is the total energy of a particle having its de Broglie wave of frequency  $\nu$ , circular frequency  $\omega$ , wave length  $\lambda$  and momentum  $p$ ,  $h = 6.62607015 \cdot 10^{-34}$  J·s is the Planck's constant,  $\hbar = h/2\pi$ .

The one-dimensional wave equation of a wave of magnitude  $\Psi$  is a partial differential equation

$$\frac{1}{v_p^2} \frac{\partial^2 \Psi}{\partial t^2} = \frac{\partial^2 \Psi}{\partial x^2} \quad (1)$$

$t$  and  $x$  denote time and position on the  $Ox$  axis.

### Key steps in derivation of the Schrödinger equation from the wave equation

The key steps leading to derivation of the Schrödinger equation are:

- **Computing of the wave phase velocity  $v_p$  of a particle** having total energy  $E$ , potential energy  $V$ , mass  $m$  and wave length  $\lambda$  using the de Broglie hypothesis and Planck's formula for the energy of quanta
- **Forming a possible solution  $\Psi(x, t)$  of the wave equation (1)**
- **Computing the second derivatives of solution  $\Psi(x, t)$  with respect to time and spatial coordinate** and inserting the computed derivatives into the wave equation (1) with already determined phase velocity  $v_p$ .
- **Substituting phase velocity and second derivatives computed in previous steps to the wave equation (1)**  
After the above operations the time independent one-dimensional Schrödinger equation becomes derived.

## The derivation of Schrödinger equation

1. Computing phase velocity  $v_p$  of the de Broglie wave of a particle

$$\begin{aligned} E - V &= \frac{1}{2}mv_p^2 = \frac{p^2}{2m} \\ 2m(E - V) &= m^2v_p^2 = p^2 \\ \lambda &= \frac{h}{p} = \frac{h}{[2m(E - V)]^{1/2}} \\ v_p &= \lambda/T = \lambda\nu = \frac{h\nu}{[2m(E - V)]^{1/2}} = \frac{E}{[2m(E - V)]^{1/2}} \end{aligned} \quad (2)$$

2. Forming a possible general solution of the wave equation (1) as product of functions  $e^{i\omega t}$  and  $\varphi(x)$  depending on time  $t$  and spatial  $x$  co-ordinate

$$\Psi = e^{i\omega t}\varphi(x) = e^{i(E/\hbar)t}\varphi(x)$$

3. Computing the second partial derivatives of the solution of equation (1) with respect to time  $t$  and  $x$  coordinate

$$\frac{\partial^2 \Psi}{\partial t^2} = -\frac{E^2}{\hbar^2}e^{i(E/\hbar)t}\varphi(x) \quad (3)$$

$$\frac{\partial^2 \Psi}{\partial x^2} = e^{i(E/\hbar)t}\frac{\partial^2 \varphi(x)}{\partial x^2} \quad (4)$$

4. Inserting (2), (3) and (4) into equation (1)

After few rearrangements the time independent one-dimensional Schrödinger equation emerges

$$-\frac{\hbar^2}{2m}\frac{\partial^2 \varphi(x)}{\partial x^2} + V(x)\varphi(x) = E\varphi(x) \quad (5)$$

## Applications of the Schrödinger equation to molecular oscillations

- **Harmonic oscillator** described and solved by E. Schrödinger in 1926
- **Modal equations of VSCF method** first proposed by J. M. Bowman in [1] shown here for two harmonic coupled oscillators

$$[h_1 + \langle \beta_{i_\beta}(Q_2) | V_c(Q_1, Q_2) | \beta_{i_\beta}(Q_2) \rangle - \varepsilon_{i_\alpha}] \alpha_{i_\alpha}(Q_1) = 0 \quad (6)$$

$$[h_2 + \langle \alpha_{i_\alpha}(Q_1) | V_c(Q_1, Q_2) | \alpha_{i_\alpha}(Q_1) \rangle - \varepsilon_{i_\beta}] \beta_{i_\beta}(Q_2) = 0$$

Vibrational Self-Consistent Field (VSCF) method has been applied by us to non-linear coupling of three harmonic oscillators of different oscillational frequencies in hydrogen-bonded crystalline uracil and 1-methyl-uracil and their deuterium substituted derivatives in order to compute and explain the subtle structure of N—H and N—D stretching oscillations in the Infra-Red absorption spectra.

## Schrödinger equation applied to molecular electronic structure

### Uracil dimer differential electron density

Uracil dimer differential electron density has been calculated according to the formula proposed by Bader and Daudel:  $\rho_{diff}(AB) = \rho(AB) - \rho(A) - \rho(B)$  where AB denotes the molecular complex and A, B denote its molecules. The differential electron density informs about the flows of electron density that occur in the inter-nuclear regions after interactions between the components of the complex occur.

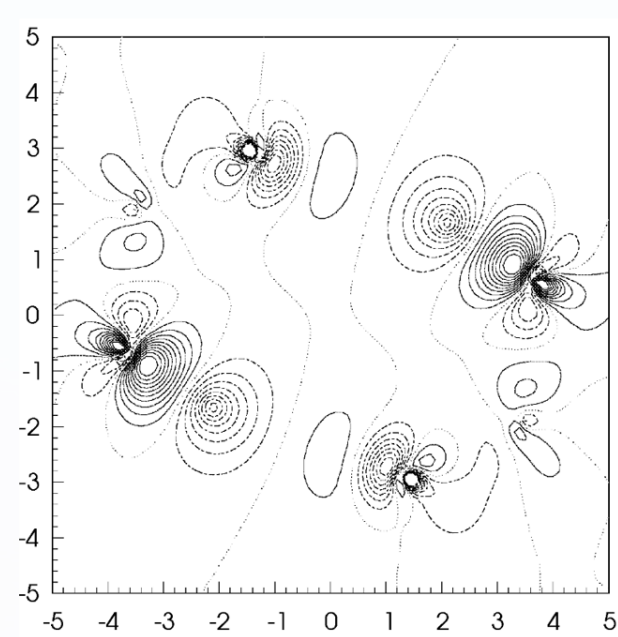


Figure 2. Uracil dimer differential electron density  $\rho_{diff}$  calculated in 6-31G\*\* basis set using RHF ab initio method. N—H ... O pairs of hydrogen bonds are visible. Solid lines indicate contours  $\rho_{diff} > 0$  while dashed lines indicate contours  $\rho_{diff} < 0$ . Both axes have the bohr as a unit of length.

A differential electron density greater than zero characterizes regions in which, due to interactions between parts of the complex electron density increases. Similarly, a negative value of differential electron density indicates an outflow of electrons from a specific area.

### Inter-molecular hydrogen bonds oscillations selection rules

Two types of inter-molecular oscillations occur: the translational oscillations and rotational oscillations. Hydrogen bond oscillations selection rules in Infra-Red absorption and Raman scattering spectroscopies have been determined using group theory methods for the uracil dimer of  $C_{2h}$  point symmetry.

Table 1. Symmetry types of inter-molecular vibrations of uracil dimer of point symmetry  $C_{2h}$

symmetry type	inter-molecular vibrations	
	translational	rotational
$A_g$	2	0
$B_g$	1	0
$A_u$	0	2
$B_u$	0	1

Inter-molecular vibrations of type  $A_g$  and  $B_g$  are Raman scattering spectroscopy active; vibrations of type  $A_u$  and  $B_u$  are Infra-Red absorption spectroscopy active.

## References

- [1] J. M. Bowman. The self-consistent-field approach to polyatomic vibrations. *Accounts of Chemical Research*, 19:202–208, 1986.
- [2] Paweł Piskorz and Marek J. Wójcik. Ab initio calculations of hydrogen-bonded dimers of uracil and 1-methyluracil. *Journal of Molecular Structure: THEOCHEM*, 332(3):217–223, 1995.
- [3] Paweł Piskorz and Marek J. Wójcik. Application of the vscf theory to coupled vibrations in hydrogen-bonded systems. *Polish Journal of Chemistry*, 72(2):387–395, 1998.