

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 ν , circular frequency ω , wave length λ 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 Ψ 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 λ 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

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

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.

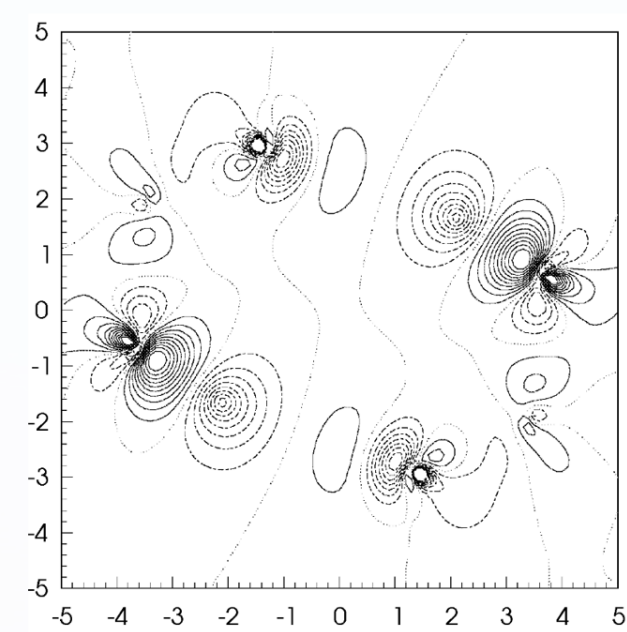


Figure 2. Uracil dimer differential electron density ρ_{diff} calculated in 6-31G** basis set using RHF ab initio method. N—H ... O pairs of hydrogen bonds are visible. Solid lines indicate contours $\rho_{diff} > 0$ while dashed lines indicate contours $\rho_{diff} < 0$. Both axes have the bohr as a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