Evaluation

- Lecture

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Evaluation

- Tutorial

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Atoms

Hydrogen atom

The Schrödinger equation as a wave equation

- Schrödinger equation
- Box potential
- Harmonic oscillator
- Orbital angular momentum
- Rotation of a diatomic molecule
- Schrödinger equation of the hydrogen atom
- normal Zeeman effect
- Dia- and paramagnetism

Schrödinger equation of the hydrogen atom 1

the hydrogen atom consists of an electron bound to a proton

Hamilton function

$$\underline{H = \frac{\vec{p}^{\,2}}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}}$$

Hamilton operator $(\vec{p} \to -i\hbar\nabla)$

$$\boxed{\hat{H} = -\frac{\hbar^2\nabla^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}}$$

Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\,\psi$$

Schrödinger equation of the hydrogen atom 1 Comment

The underlined equation gives the Hamilton function of a classical particle with potential energy.

The potential energy of the electron is caused by the electric field of the proton.

The Hamilton operator results when the momentum in the Hamilton function is replaced by the momentum operator $-\mathrm{i}\hbar\nabla$.

The equation in the bottom line shows the Schrödinger equation again.

Schrödinger equation of the hydrogen atom 2

Ansatz to solve the time-dependent Schrödinger equation

$$\underline{\psi(\vec{r},t) = \varphi(\vec{r})e^{-iEt/\hbar}}$$

time independent Schrödinger equation

$$\boxed{E\varphi(\vec{r}) = \hat{H}\varphi(\vec{r})}$$

the potential energy is only a function of the radius r

$$\hat{H} = -\frac{\hbar^2\nabla^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

→ spherical coordinates for the Laplace operator

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}$$

(https://de.wikipedia.org/wiki/Laplace-Operator)

Schrödinger equation of the hydrogen atom 2 Comment

Since the Hamilton operator does not explicitly contain the time, the solution of the Schrödinger equation is a standing wave.

The equation underlined shows the standing wave. The spatial and temporal variations are described by different functions.

This results in the time-independent Schrödinger equation.

Spherical coordinates can be used for the Laplace operator, since the potential energy of the electron only depends on the distance *r* to the atomic nucleus, i.e. to the proton.

Schrödinger equation of the hydrogen atom 3

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2\nabla^2}{2m} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \\ &= -\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) \\ &\quad + \frac{1}{2mr^2}(-\hbar^2)\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\} \\ &\quad - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}\end{aligned}$$

Eigenvalue equation of the angular momentum operator

$$\hat{\vec{L}}^2 Y_{\ell,m}(\theta,\varphi) = -\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right\}Y_{\ell,m}(\theta,\varphi) = \hbar^2\ell(\ell+1)Y_{\ell,m}(\theta,\varphi)$$

Schrödinger equation of the hydrogen atom 3 Comment

The Hamilton operator can thus be broken down into a radial and an angle-dependent part.

The angle-dependent part is determined by the square of the angular momentum.

This contribution is marked in blue in the equation outlined in red.

The last line gives the eigenvalue equation for the square of the angular momentum.

The eigenfunctions of the squared angular momentum operator are the spherical harmonics $Y_{\ell,m}(\theta,\varphi)$ and the ℓ quantum number takes on the values 0, 1, 2 etc. .

Schrödinger equation of the hydrogen atom 4

time independent Schrödinger equation of the hydrogen atom

$$E\varphi(\vec{r}) = \left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\hat{\vec{L}}^2}{2mr^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \right)\varphi(\vec{r})$$

ansatz for the wave function

$$\varphi(\vec{r}) \quad \rightarrow \quad \varphi_{n,\ell,m}(r,\theta,\varphi) = Y_{\ell,m}(\theta,\varphi)R_{n,\ell}(r)$$

eigenvalue equation for the radial wave function

$$\boxed{E_{n,\ell}R_{n,\ell}(r) = \left(-\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{\ell(\ell+1)\hbar^2}{2mr^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r} \right)R_{n,\ell}(r)}$$

$$E = E_{kin} + E_{pot} = \frac{\vec{p}_r^{\,2}}{2m} + \frac{\vec{L}^2}{2mr^2} + E_{pot}$$

Schrödinger equation of the hydrogen atom 4 Comment 1

The equation underlined in red gives the Schrödinger equation with the angular momentum operator.

The orbital wave function $\varphi(\vec{r})$ can be decomposed into the spherical harmonic $Y_{\ell,m}$ and a radial function that only depends on r.

The solution of the Schrödinger equation shows that the radial wave function depends on the principal quantum number n and on the quantum number ℓ of the angular momentum.

The equation outlined in red shows the eigenvalue equation for the radial wave function.

The angular momentum operator is replaced by its eigenvalues $\ell(\ell+1)\hbar^2$.

Schrödinger equation of the hydrogen atom 4 Comment 2

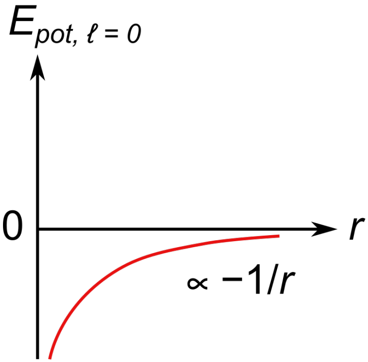
For comparison, the last equation shows the classical energy of a particle moving in a radial potential.

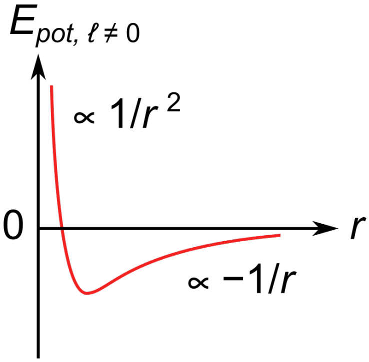
The similarity and the difference between the classical law of conservation of energy and the time-independent Schrödinger equation is obvious.

Schrödinger equation of the hydrogen atom 5

the effective potential energy

$$\boxed{E_{pot,\ell}(r) = \frac{\hbar^2 \ell(\ell+1)}{2mr^2} - \frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}}$$





Schrödinger equation of the hydrogen atom 5 Comment 1

The potential energy due to the Coulomb potential of the nucleus and the kinetic energy due to the angular momentum of the electron together form an effective potential energy.

When the angular momentum is zero, there is only the attractive force due to the nucleus, i.e. the proton in case of the hydrogen atom.

The electron can penetrate the nucleus without resistance.

In classical physics, the electron would perform an oscillating motion through the nucleus.

The energy oscillates between the radial kinetic energy of the electron and the potential energy due to the attractive force of the nucleus.

Schrödinger equation of the hydrogen atom 5 Comment 2

In classical physics, the electron would lose energy through the emission of electromagnetic radiation.

The Schrödinger equation shows that no electromagnetic radiation can be emitted due to this motion.

The probability density to find the electron results from the square of the wave function.

The wave function itself assumes a finite value for $r \rightarrow 0$ and the probability of finding the electron within the atomic nucleus is not zero.

Although the angular momentum is zero, application of the uncertainty principle shows that the particle cannot move in a straight line since the uncertainty of momentum perpendicular to the line of motion would be zero.

Schrödinger equation of the hydrogen atom 5 Comment 3

Since the spherical harmonic of an s orbital is a constant, all directions of motion are equally likely.

If the angular momentum of the electron is not equal to zero, the effective potential energy for $r \to 0$ becomes very large due to the angular momentum of the electron.

A strong repulsive force acts between the atomic nucleus and the electron, since the centrifugal force becomes very strong at small distances from the atomic nucleus.

The wave function of the electron becomes zero for $r \to 0$.

The probability of finding the electron in or near the nucleus is zero for electrons with angular momentum.

Schrödinger equation of the hydrogen atom 5 Comment 4

There is a big difference between so-called s-electrons and electrons with $\ell \neq 0$: s-electrons penetrate the nucleus, while electrons with angular momentum are kept away from the nucleus due to the centrifugal force.

This is why s-electrons are particularly sensitive to the properties of the nucleus.

Schrödinger equation of the hydrogen atom 6

radial wave functions

$$\boxed{R_{n,\ell}(r) = f_{n,\ell}(r) \cdot e^{-r/na_B}}$$

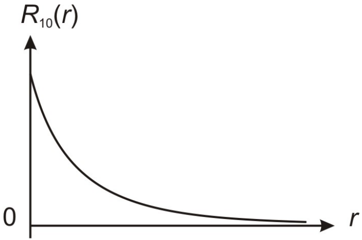
$f_{n,\ell}(r)$ denotes a polynomial which is determined by the quantum numbers n and ℓ

for $n = 1$ and $\ell = 0$ is the radial wave function an exponential function

$$R_{10}(r) \propto e^{-r/a_B}$$

and

$$\boxed{E_1 = -13.6\,\text{eV}}$$



Schrödinger equation of the hydrogen atom 6 Comment 1

Now the radial wave functions have to be considered.

The radial wave function is the product of an exponential function and a polynomial.

This is reminiscent of the harmonic oscillator solution.

The polynomials are well known in mathematics and are called Laguerre polynomials.

The polynomials depend on the quantum number n and ℓ.

The formula outlined in red gives the general solution of the radial Schrödinger equation.

Schrödinger equation of the hydrogen atom 6 Comment 2

The radial wave function of the ground state is a simple exponential function.

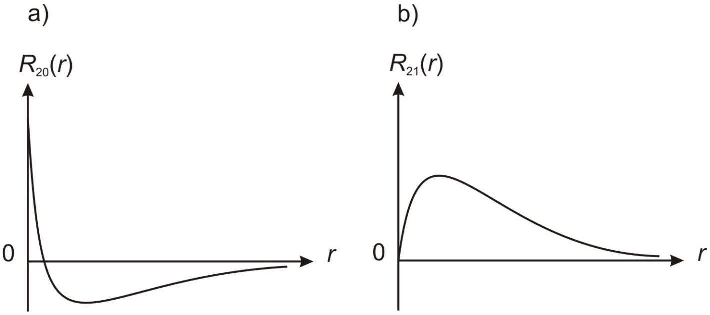
The solution of the Schrödinger equation shows that the decay length of the exponential function is given by the Bohr radius.

The numerical value -13.6 eV results for the energy of the ground state, which agrees perfectly with the experimental result.

The principal quantum number takes on the value $n = 1$ and there is no rotational energy i.e. $\ell = 0$.

Schrödinger equation of the hydrogen atom 7

for $n = 2$ there is one s orbital and three p orbitals



$$R_{21}(r) \propto r e^{-r/2a_B} \quad \text{and} \quad E_2 = -\frac{13.6\,\text{eV}}{2^2}$$

$$R_{20}(r) \propto (1 - \frac{r}{2a_B}) e^{-r/2a_B} \quad \text{and} \quad E_2 = -\frac{13.6\,\text{eV}}{2^2}$$

Schrödinger equation of the hydrogen atom 7 Comment 1

If one increases the angular momentum to $\ell = 1$, one finds a solution of the Schrödinger equation, if one multiplies the exponential function with the distance r between electron and proton.

Due to the centrifugal force the radial wave function vanishes for $r \to 0$.

The first underlined equation gives the result of the calculation.

The decay length of the exponential function is twice the Bohr radius and the energy is equal to $-13.6/2^2$.

This is the energy of the first excited state with the principal quantum number $n = 2$.

$\ell = 1$ denotes a p orbital and there are three eigenfunctions with $m = -1, 0, +1$.

Schrödinger equation of the hydrogen atom 7 Comment 2

If ℓ is reduced to zero for an s-electron, the radial wave function must start at $r = 0$ with a finite value.

Since the energy due to the angular momentum is zero, the energy of the radial movement has to be increased by adding a node to the standing wave.

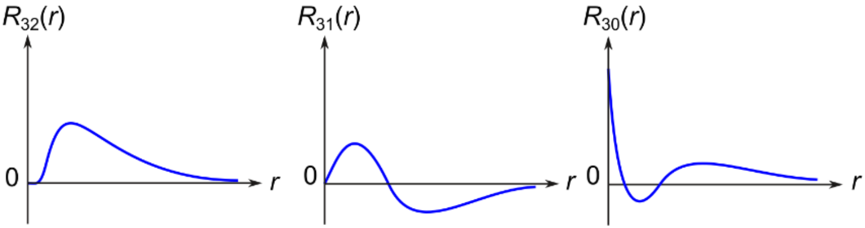
The second underlined equation shows the polynomial that results from solving the Schrödinger equation.

The energy of the s orbital is the same as that of the p orbital, i.e.
$E_{\mathrm{n}=2} = -13.6/2^2$ eV.

Both the s- and the p orbital have the same energy.

Schrödinger equation of the hydrogen atom 8

for $n = 3$ there is one s orbital, three p orbitals and five d orbitals



$$\underline{R_{32}(r) \propto r^2 e^{-r/3a_B}} \quad \text{and} \quad \boxed{E_3 = -\frac{13.6\,\text{eV}}{3^2}}$$

$$R_{31}(r) \propto \frac{r}{a_B}\left(1 - \frac{r}{6a_B}\right) e^{-r/3a_B} \quad \text{and} \quad R_{30}(r) \propto \left(27 - \frac{18r}{a_B} + \frac{2r^2}{a_B^2}\right) e^{-r/3a_B}$$

Schrödinger equation of the hydrogen atom 8 Comment 1

If the angular momentum is increased to $\ell = 2$, one can start with the underlined wave equation.

The exponential function is multiplied by r^2.

The solution of the Schrödinger equation shows that the decay length of the exponential function is given by $3a_\mathrm{B}$.

The formula outlined in red gives the energy of this wave function.

The principal quantum number of this solution is $n = 3$ and the energy of the orbital is $-13.6/3^2$ eV.

Schrödinger equation of the hydrogen atom 8 Comment 2

If ℓ is reduced to 1, the radial energy has to be increased by adding a node.

The radial wave function has to start at zero, since the effective potential for $r \to 0$ becomes strongly repulsive.

The solution of the Schrödinger equation is the wave function R_{31} and the energy is also $-13.6/3^2$ eV.

For the s-electron the radial wave function has to start with a finite value for $r = 0$ and a second node has to be added to increase the radial energy.

The wave function R_{30} is the solution and the energy is also $-13.6/3^2$ eV.

Schrödinger equation of the hydrogen atom 9

probability to find the electron within the volume *dV* is

$$\underline{\psi(\vec{r})\psi(\vec{r})^* dV}$$

volume element in spherical coordinates

$$\underline{dV = r^2 dr \sin\theta d\theta d\varphi}$$

probability when using spherical coordinates

$$\boxed{\psi\psi^* dV = r^2 R_{n,\ell}^2 dr \cdot Y_{\ell,m} Y_{\ell,m}^* \sin\theta d\theta d\varphi}$$

usually $\underline{r^2 R_{n,\ell}^2}$ is plotted

Schrödinger equation of the hydrogen atom 9 Comment

The first underlined equation gives the probability of finding the electron in the volume element *dV*.

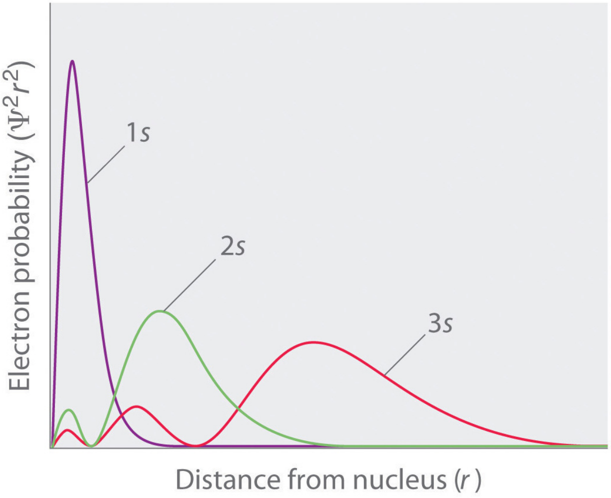
The second underlined equation gives the volume element when spherical coordinates are used.

The equation outlined in red gives the probability for a volume element in spherical coordinates if the wave functions of the hydrogen atom are used.

The probability can be broken down into a radial and an angle-dependent component.

The last underlined equation gives the radial probability density to find the electron within the interval *dr*.

Schrödinger equation of the hydrogen atom 10

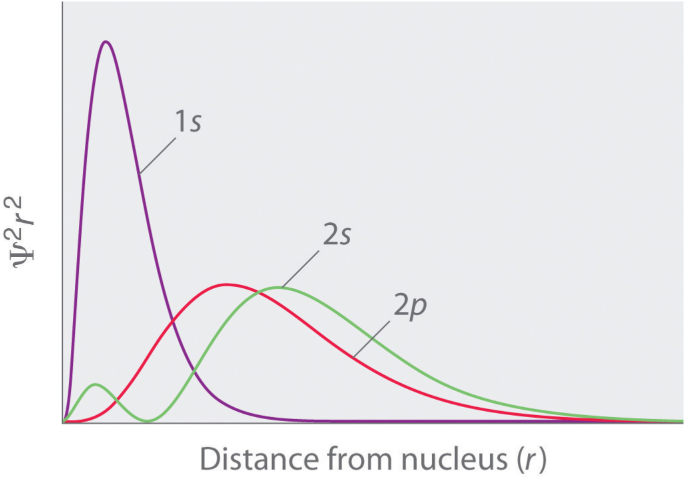


Schrödinger equation of the hydrogen atom 10 Comment

The figure shows the radial probability density of the ground state and the first and second excited s orbital.

The decay length of the exponential function is $1a_B$ for $n = 1$, $2a_B$ for $n = 2$ and $3a_B$ for $n = 3$.

Schrödinger equation of the hydrogen atom 11



Schrödinger equation of the hydrogen atom 11 Comment

The figure compares the radial probability density for the ground state and the s and p orbital of the first excited state.

The maximum of the probability density of the 2s orbital is somewhat shifted to larger *r* values than for the 2p orbital.

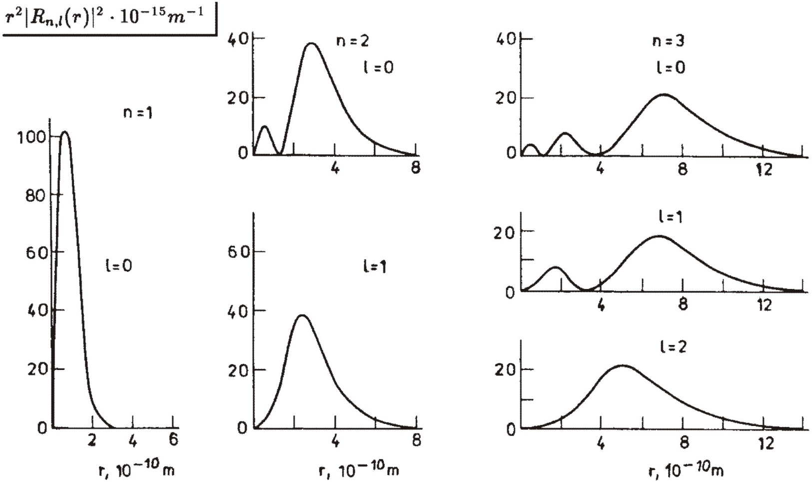
This effect becomes more pronounced with increasing *n* quantum number.

This is shown in the following figure.

In the s orbital, all of the energy is due to the radial movement, while in the other orbitals a fraction of the energy is due to the rotational movement.

The more energy there is in the radial movement, the further the maximum of the wave function shifts away from the atomic nucleus.

Schrödinger equation of the hydrogen atom 12



Schrödinger equation of the hydrogen atom 12 Comment

The figure compares the radial probability density of the ground state and the first and second excited states.

Schrödinger equation of the hydrogen atom 13

energy eigenvalues:

(in agreement with experiment)

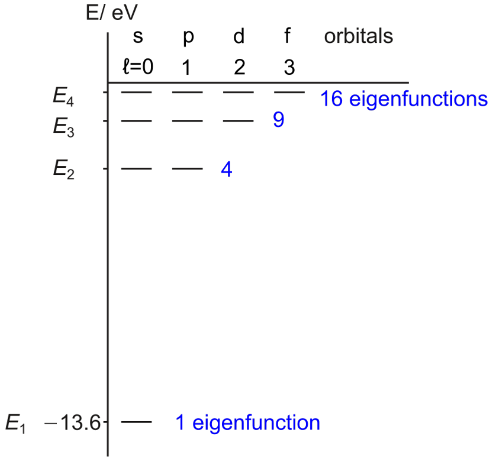
$$\boxed{E_n = -13.6\,\mathrm{eV}\frac{1}{n^2}}$$

with

$$\boxed{n = 1, 2, \ldots}$$

and

$$\boxed{\ell < n}$$



Schrödinger equation of the hydrogen atom 13 Comment 1

On this page I summarize the results of the Schrödinger equation for the hydrogen atom.

The Hamilton operator contains the kinetic energy of the electron and the potential energy due to the movement in the electric field of the nucleus.

The first equation outlined in red gives the total energy, which is in perfect agreement with the experimental results of Balmer, Lyman, Paschen, etc.

The second and third formulas outlined in red give the conditions for the principal quantum number and the angular momentum quantum number ℓ.

The figure shows the resulting energy level diagram.

Schrödinger equation of the hydrogen atom 13 Comment 2

The energy level scheme is similar to that of the alkali metals.

There are the energy levels of the side series, the principal series, the diffuse series, and the fourth forth series.

s, p, d, f now denote the quantum number of the orbital angular momentum of the electron.

In contrast to the energy levels of the alkali metals, the energy levels of the hydrogen atom have the same energy with the same principal quantum number. (If you take a closer look, small energy shifts can also be observed in the hydrogen atom.)

Schrödinger equation of the hydrogen atom 13 Comment 3

The reason for this is the $1/r$ dependence of the potential energy of the electron in the electric field of the proton.

In the case of the valence electron, the electrical potential is not only determined by the nucleus, but also by the shielding of the atomic nucleus by the core electrons and deviates from the $1/r$ dependence.

The energy of the valence electron therefore depends not only on the principal quantum number n but also on the angular momentum quantum number ℓ.

Revision

Summary in Questions

1. Give the quantum numbers which characterize an orbital of the hydrogen atom.
2. Give all quantum number of an orbital with the main quantum number $n = 3$.
3. Sketch the radial wave functions with the quantum numbers $n = 4$, $\ell = 3$ and $n = 4$, $\ell = 0$.
4. Give arguments for these plots.
5. Sketch the radial probability density for the quantum numbers $n = 4$, $\ell = 0$.
6. Show that the wave function e^{-r/a_B} is a solution of the Schrödinger equation of the hydrogen atom.
7. Calculate the numerical value of the corresponding eigenvalue.