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# Spectral Properties of Confined Systems

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## History

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*Bemerkung zur Quantelung des harmonischen Oszillators im Magnetfeld*,  
Z. Phys. **47** (1928) 446-448.  
A study of the confinement by a uniform magnetic field – formally equivalent to a Hooke's-law-type confinement.
- C. G. Darwin,  
*The Diamagnetism of the Free Electron*,  
Proc. Cambridge Philos. Soc. **27** (1930) 86-90.  
An extension of the earlier work by Fock.
- A. Sommerfeld und H. Welker,  
*Künstliche Grenzbedingungen beim Keplerproblem*,  
Ann. Phys. **32** (1938) 56-65.  
A study of the hydrogen atom confined in the center of a spherical impenetrable cage. A prototype for many later studies of confined atoms (also referred to as *compressed atoms*).
- E. Schrödinger,  
*Further studies on solving eigenvalue problems by factorization*,  
Proc. R. Irish Acad. A **46** (1940) 183-206.  
An analytically solvable model of the hydrogen atom confined in a cotangent-type potential.



## History

- N. R. Kestner and O. Sinanoğlu, *Study of electron correlation in helium-like systems using an exactly soluble model*, Phys. Rev. **128** (1962) 2687.  
The first study of the only known *exactly soluble* system which describes two electrons interacting with Coulomb forces: two electrons confined in an external harmonic oscillator potential.
- J. Jortner, N. R. Kestner, S. A. Rice, and M. H. Cohen, *Study of the properties of an excess electron in liquid helium. The nature of the electron-helium interaction*, J. Chem. Phys. **43** (1965) 2614-2625.  
A study of the properties of an electron confined in a bubble formed in liquid helium.
- R. J. White and W. B. Brown, *Perturbation theory of the Hooke's law model for the two-electron atom*, J. Chem. Phys. **53** (1970) 3869-3879; 3880-3886.  
A study of two interacting electrons confined in an external harmonic oscillator potential.



## Relation to experiment

- Quantum dots
- Atoms and molecules confined
  - In liquid helium,
  - In helium droplets,
  - On surfaces,
  - In zeolite molecular sieves,
  - In fullerenes.
- Quark models of nucleons and mesons.



## Models of confinement

Types of confining potentials:

- Infinite (unpenetrable) rectangular wells,
- Finite rectangular wells,
- Cotangent-type and related potentials,
- Harmonic oscillator-type potentials,
- Power potentials,
- Limited from above (finite depth) potentials.



## Models of confinement

Levels of accuracy in describing interactions between particles:

- Interactions between particles are neglected.
- Interactions between electrons are included at the Hartree-Fock level.
- A complete description of electron correlation effects is included.



## Quantum chemistry in confinement

The  $N$ -electron Schrödinger equation  
for a confined Born-Oppenheimer system:

$$H\Psi = E\Psi,$$

where

$$H(\mathbf{r}) = T(\mathbf{r}) + V(\mathbf{r}) + W(\mathbf{r}) + G(\mathbf{r})$$

$$\mathbf{r} \equiv \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\},$$

$T$  – kinetic energy,

$V$  – nuclear attraction potential,

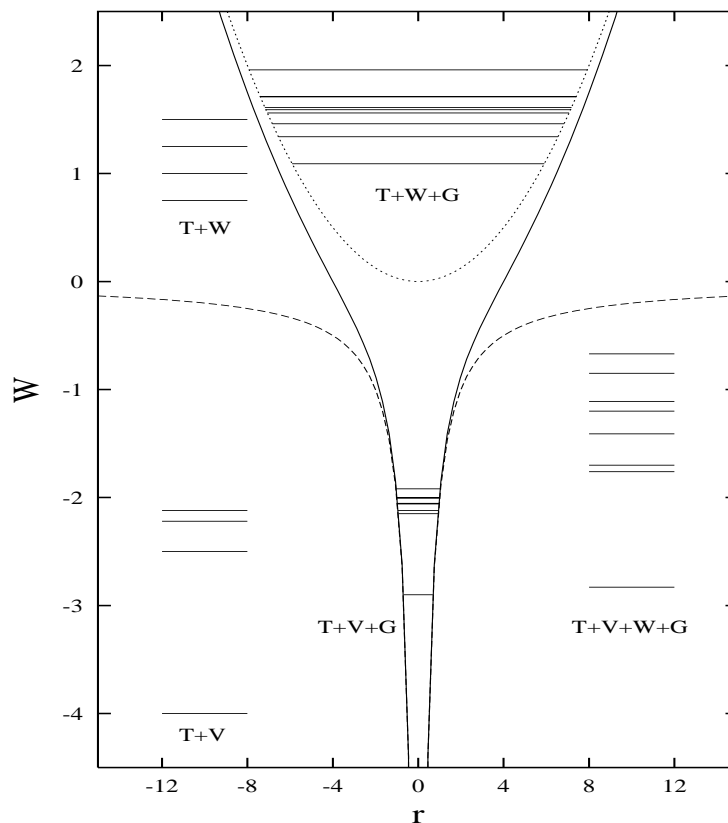
$W$  – confinement potential,

$G$  – electron interaction potential.

In this work

$$W(\mathbf{r}) = \frac{\omega^2}{2} \sum_{i=1}^N r_i^2$$





## Interplay of different terms in the Hamiltonian

(All energies are in atomic units)

Broken line:	Free helium atom potential	$V(r) = -2/r;$
Dotted line:	$\omega = 1$ confinement potential	$W(r) = r^2/2;$
Solid line:	Total external potential	$V(r) + W(r);$
Horizontal lines:	Eigenvalues of the two-electron Hamiltonians.	



## Solving the Schrödinger equation for a confined system.

- Case-specific methods have been developed in various areas of physics.
- Universal methods have been developed in quantum chemistry:
  - No correlation: Hartree-Fock (HF).
  - Electron correlation:
    - \* Configuration interaction (CI)
    - \* Coupled clusters (CC)
    - \* Many-body perturbation theory (MBPT)

The calculations are performed by expanding the one-electron orbitals in a basis of properly selected primitive Gaussian functions.

The effect of the confinement is included by adding the nuclear attraction and the confinement potential to form a general external potential.

No essential change in the formulation of the methods used in computational chemistry is necessary.



## OpenMol

**OpenMol** is an object oriented program developed in the Molecular Physics Group at the Max-Planck-Institute for Astrophysics, Garching, Germany. It provides, among others, all computational tools necessary to solve the Schrödinger equation for a confined atom or a confined molecule and to analyze the solution.

Properties which may be studied include, among others:

- structure of spectra,
- molecular geometry,
- electron density,
- electric moments,
- electric polarizabilities,
- transition probabilities,
- effects of confinement on all these properties.



## Gaussian basis set (1)

The basis set has been designed to describe:

- the atomic core electrons with densities strongly contracted in the vicinity of the nucleus (large exponent Gaussians),
- the excited state electrons with diffuse densities (small exponent Gaussians) and the effects
- of the confinement (exponents determined by the strength of the confinement).



## Gaussian basis set (2)

An even-tempered universal set of primitive Gaussians has been used. The exponents of the primitive Gaussians have been generated by using the formula:

$$\zeta_{k,\ell} = \alpha_\ell \beta_\ell^k, \quad k = 0, 1, 2, \dots, m_\ell \quad (1)$$

The asymptotic behaviour of the one-electron wavefunction describing a confined electron is given by:

$$\phi(x) = \exp \left[ -(\omega^{1/2}|x|)^{n+1}/(n+1) \right]. \quad (2)$$

In the case of  $n = 1$  the exact solution of the confined problem may be expressed in terms of Gaussian functions.



## **Two-electron systems confined by harmonic-oscillator-type potentials**

The Schrödinger equation for a confined system may be transformed in two, formally equivalent, ways. Depending on the choice of the zeroth-order approximation, the unperturbed Hamiltonian may be selected as:

1. Describing non-interacting electrons moving in the field of the nucleus – model for weak confinements.
2. Describing non-interacting electrons in the confining potential – model for strong confinements.



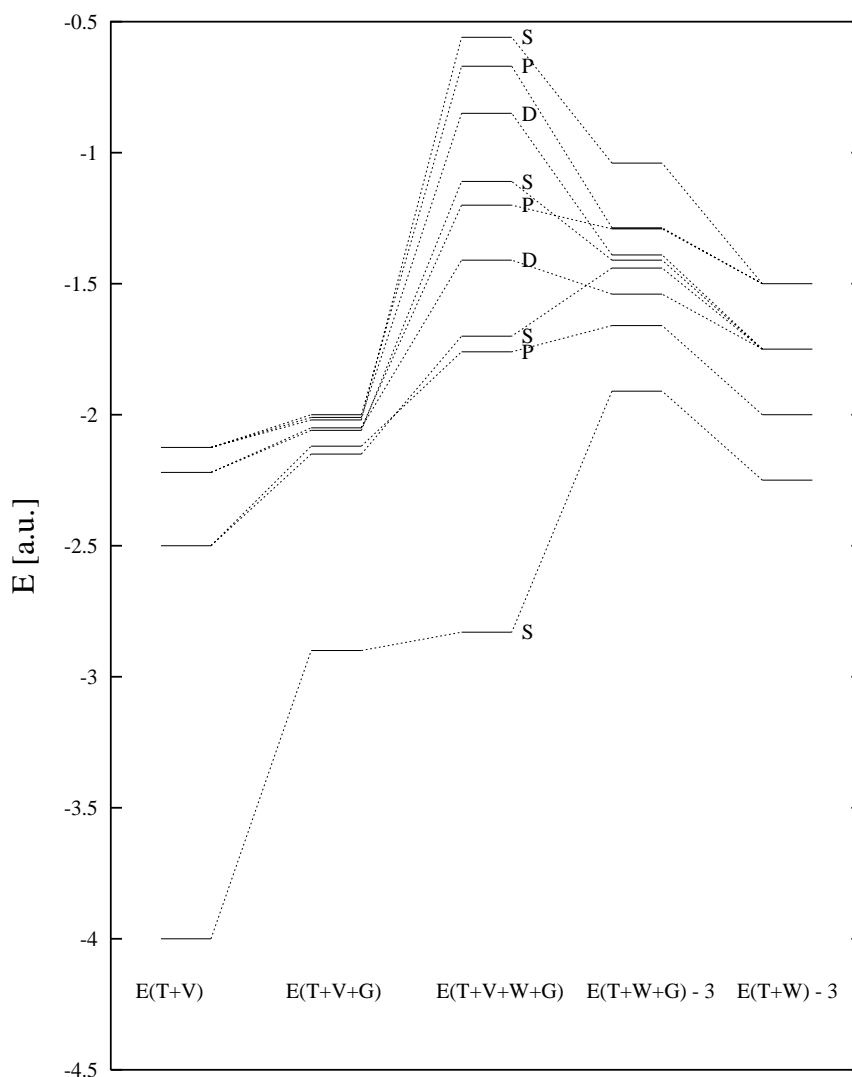
## Spectral Characteristics

The spectrum of a confined atom differs fundamentally from that of a free atom.

- If the confining potential is positive definite then all energy levels of the confined system are shifted towards higher energies.
- If the confinement is described by a potential unbounded from above then there exists no continuum.
- The energy of the electronic ground state of a confined atom increases with increasing strength of the confinement faster than the ground state energy of its positive ion.
- The ordering of atomic and molecular energy levels changes due to confinement.



## Correlation Diagram (5)



Correlation diagram  
 between the lowest singlet energy levels  
 of two electrons confined by  
 the nuclear attraction and by the Hooke's law  
 potential





## Correlation Diagram (1)

The Schrödinger equation has well known analytical solutions for two extreme cases, corresponding to:

$$H_0^Z = T + V$$

and to

$$H_0^\omega = T + W,$$





### Correlation Diagram (3)

The eigenvalues of  $H_0^\omega$  are given by

$$E_0^\omega = \omega(\nu + 3), \quad (5)$$

where  $\nu = 2(\nu_1 + \nu_2) + \ell_1 + \ell_2 = 0, 1, 2, \dots$  with the one-electron principal quantum numbers  $\nu_1, \nu_2 = 0, 1, 2, \dots$  and the one-electron angular momentum quantum numbers  $\ell_1, \ell_2 = 0, 1, 2, \dots$ . The consecutive configuration energies  $E_0^\omega[\nu_1 \ell_1 \nu_2 \ell_2]$  are:

$$E_0^\omega[(0s)^2] = 3\omega,$$

$$E_0^\omega[0s0p] = 4\omega,$$

$$E_0^\omega[0s1s] = E_0^\omega[0s0d] = E_0^\omega[(0p)^2] = 5\omega,$$

$$E_0^\omega[0s1p] = E_0^\omega[1s0p] = E_0^\omega[0s0f] = E_0^\omega[0p0d] = 6\omega, \dots$$



## Correlation Diagram (4)

The Hamiltonian

$$H^\omega = H_0^\omega + G = T + W + G$$

describes harmonium. In its spectrum the degenerate energy levels of  $H_0^\omega$  are split due to the electron interaction. If this splitting is smaller than that due to the Hooke's law potential (i.e. if the separation between the extreme energies of the terms related to the same configuration is smaller than  $\omega$ ), then the consecutive singlet energies are:

$$E^\omega[S(0s)^2] < E^\omega[P(0s0p)] < E^\omega[D(0s0d)] < E^\omega[S(0s1s)] < E^\omega[S(0s2s)] \quad (6)$$



## Overview of the results

The following results are presented:

- A general correlation scheme between energy levels of harmonium ( $Z = 0$ ) and of helium-like atoms ( $\omega = 0$ );
- The dependence of the energy levels on  $\omega$  for harmonium, for a negative ion, for a neutral atom, and for a positive ion ( $Z = 0, 1, 2, 3$  respectively);
- The dependence of the energy levels on  $Z$  while  $Z$  and  $\omega$  are related by

$$\omega/Z^2 = k = \text{const.} \quad (7)$$

- The dependence of the energy levels on  $Z$  for fixed  $\omega$ .



## Weak confinement regime

A substitution  $\rho = Zr$  gives

$$[H_0(\rho) + X(\rho)] \Psi = \frac{E}{Z^2} \Psi,$$

where

$$H_0(\rho) = T(\rho) + V_1(\rho),$$

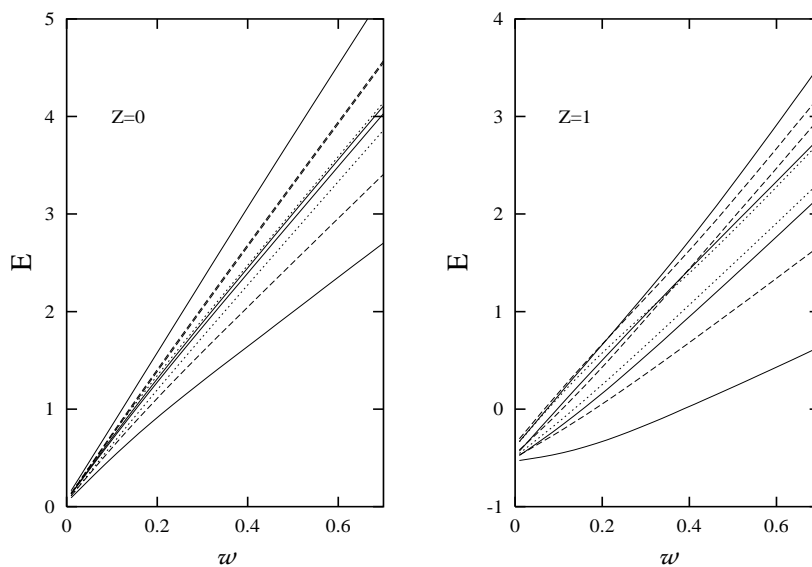
$$X(\rho) = \frac{1}{Z} G(\rho) + \left(\frac{\omega}{Z^2}\right)^2 W_1(\rho).$$

$V_1$  denotes  $V$  with  $Z = 1$

$W_1$  denotes  $W$  with  $\omega = 1$

If  $\omega \leq 1$  then

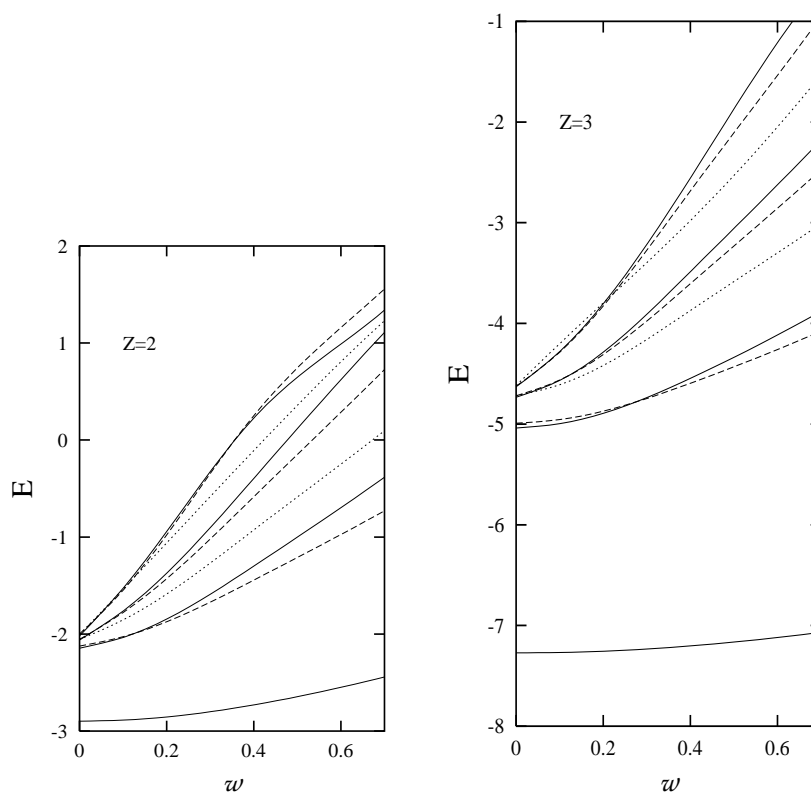
$$E = E_0(Z) + \omega^2 E_1(Z) + \omega^4 E_2(Z) + \mathcal{O}(\omega^6).$$



Singlet energy levels of two electrons ( $Z = 0$ ) and of  $H^-$  ( $Z = 1$ ) confined in the potential  $W = \frac{1}{2} \omega^2 r^2$   
(All energies are in atomic units)

Solid lines:  $^1S$   $[(1s)^2, 1s2s, 1s3s, 1s4s]$ ;  
Broken lines:  $^1P$   $[1s2p, 1s3p]$ ;  
Dotted lines:  $^1D$   $[1s3d \text{ and } 1s4d]$ .

Note the crossings of the energy levels in the case of  $Z = 1$ .  
No or weak confinement:  $E(n, \ell) < E(n, \ell + 1)$ ,  
Medium or large confinement:  $E(n, \ell) > E(n, \ell + 1)$ .



Singlet energy levels of  $He$  ( $Z = 2$ ) and  
of  $Li^+$  ( $Z = 3$ ) confined in the potential  $W = \frac{1}{2} \omega^2 r^2$   
(All energies are in atomic units)

Solid lines:  $^1S$  [(1s)<sup>2</sup>, 1s2s, 1s3s, 1s4s];  
broken lines:  $^1P$  [1s2p, 1s3p];  
dotted lines:  $^1D$  [1s3d and 1s4d].

No or weak confinement:  $E(n, l) < E(n, l + 1)$ ,  
Medium or large confinement:  $E(n, l) > E(n, l + 1)$ .





## Strong confinement regime.

A substitution  $\tilde{\rho} = \omega^{1/2} r$  gives

$$\left[ \tilde{H}_0(\tilde{\rho}) + \tilde{X}(\tilde{\rho}) \right] \Psi = \frac{E}{\omega} \Psi,$$

where

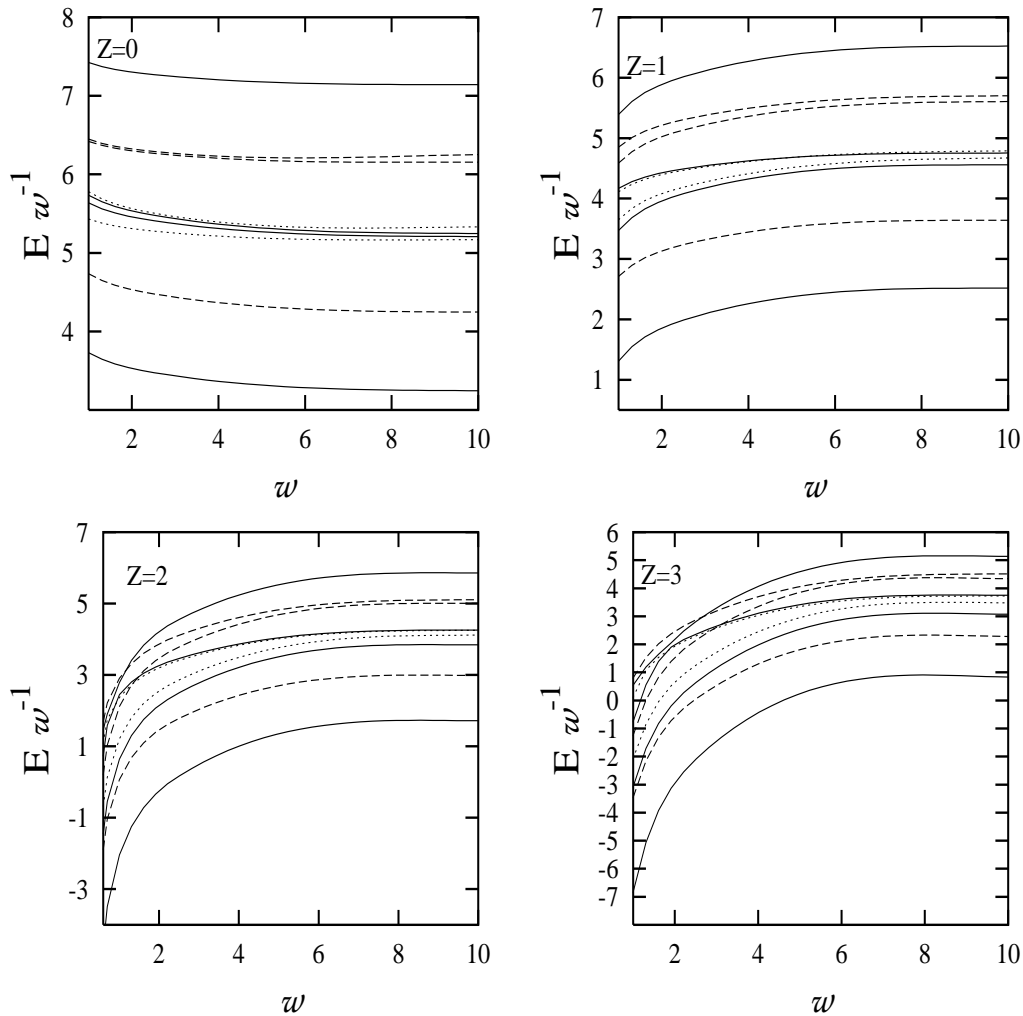
$$\tilde{H}_0(\tilde{\rho}) = T(\tilde{\rho}) + W_1(\tilde{\rho}),$$

$$\tilde{X}(\tilde{\rho}) = \frac{1}{\omega^{1/2}} [Z V_1(\tilde{\rho}) + G(\tilde{\rho})]$$

$V_1$  denotes  $V$  with  $Z = 1$   
 $W_1$  denotes  $W$  with  $\omega = 1$

If  $\omega \geq 1$  then

$$E = \omega \tilde{E}_0(Z) + \omega^{1/2} \tilde{E}_1(Z) + \tilde{E}_2(Z) + \mathcal{O}(\omega^{-1/2}).$$



Singlet energy levels of two-electron atoms with nuclear charges  $Z$  confined in a potential  $W = \frac{1}{2}\omega^2 r^2$ .  
(All energies in a.u., scaled by  $1/\omega$ )

Solid lines:  $^1S$   $[(1s)^2, 1s2s, 1s3s, 1s4s]$ ;  
broken lines:  $^1P$   $[1s2p, 1s3p]$ ;  
dotted lines:  $^1D$   $[1s3d \text{ and } 1s4d]$ .

Note energy the level crossings: for  $Z = 2$  the medium-confinement sequence  $3d < 3p < 3s < 4d$  changes to  $4d < 3s < 3p$  in the area of  $\omega \sim 1$ ; a similar behaviour appears in the case of  $Z = 3$  for  $\omega \sim 2 - 3$ .



## Coherent change of $Z$ and $\omega$ .

If  $Z$  and  $\omega$  are simultaneously changed so that

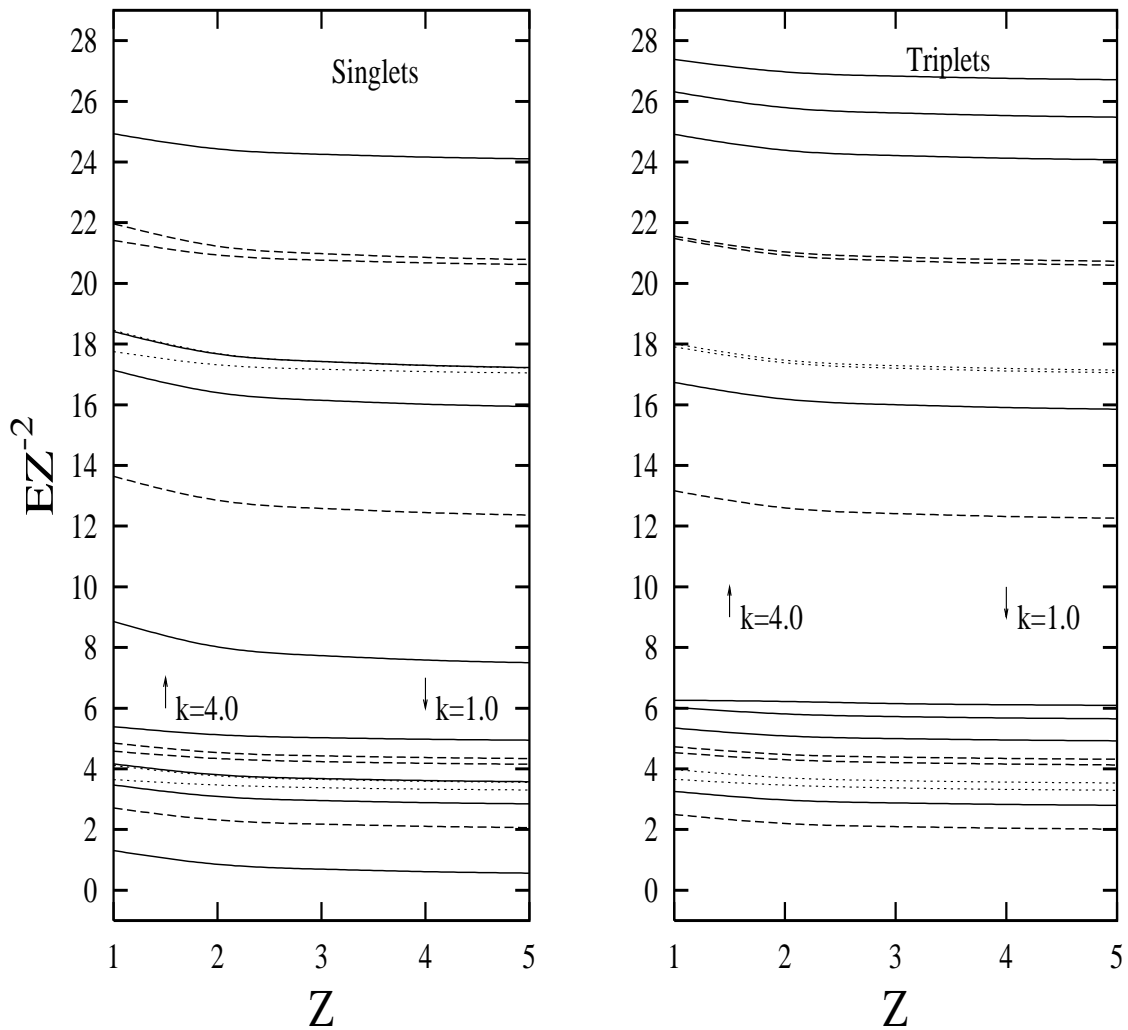
$$\frac{\omega}{Z^2} = k = \text{const},$$

all terms in the rescaled Hamiltonian, except  $G$ , remain constant.

Consequently, if the electronic interaction is neglected, then:

- The energy is strictly proportional to  $Z^2$ ,
- The values of  $\frac{E}{Z^2}$  are constant if  $k$  is constant,
- The wavefunction retains its shape: it depends upon  $Z$  and  $\omega$  only through the scaling of  $r$ .

If  $G = 0$  then the order of the one-electron energy levels and the scheme of the filling of shells remain unchanged in the whole sequence of confined atoms. Only the electron interaction  $G$  may modify the energies but its influence decreases with increasing  $Z$ .



Singlet (left fig.) and triplet (right fig.) energy levels  
of two-electron atoms

confined in harmonic oscillator potentials

$$\frac{\omega}{Z^2} = k = \text{const}, \text{ for } k = 1 \text{ and for } k = 4.$$

The consecutive  $S$ ,  $P$ ,  $D$  levels are represented,  
respectively,

by solid, broken and dotted lines.

(All energies are in atomic units)



## $Z$ – dependence of the energy levels

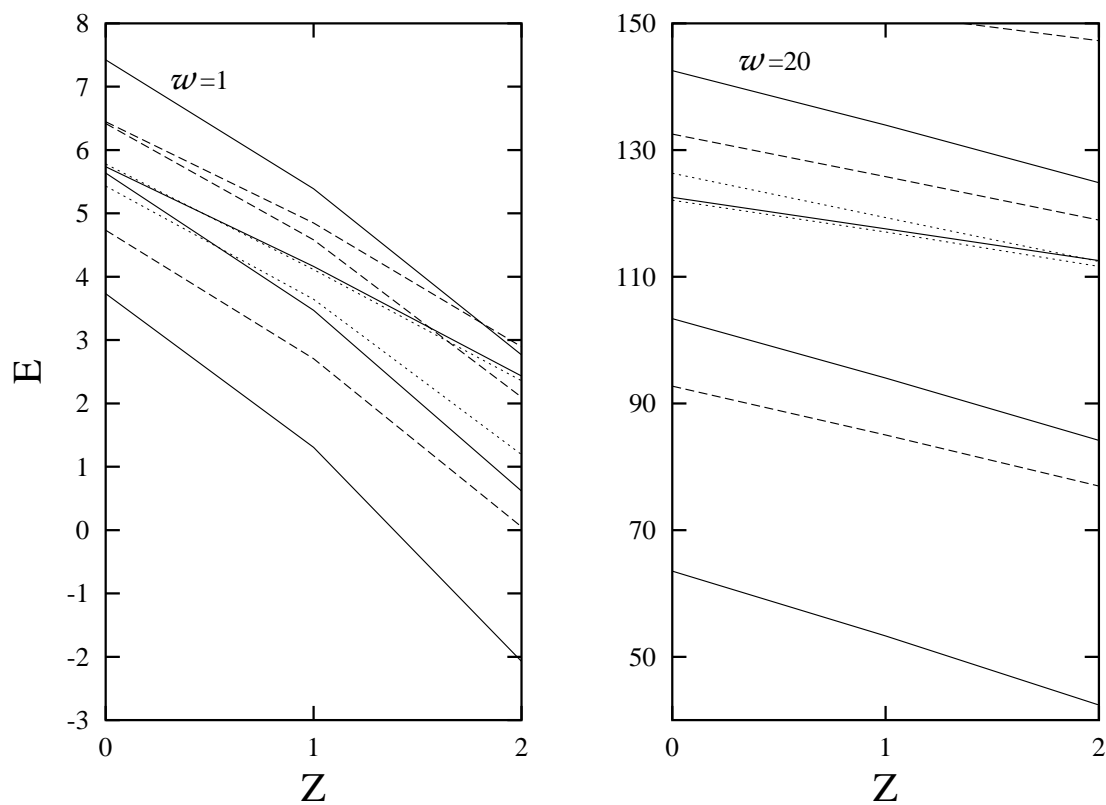
For a fixed confinement, the energies monotonously decrease with increasing  $Z$ .

The energy may be expanded as

$$E = Z^2 \mathcal{E}_0 + Z \mathcal{E}_1 + \mathcal{E}_2 + Z^{-1} \mathcal{E}_3 + \mathcal{O}(Z^{-2}).$$

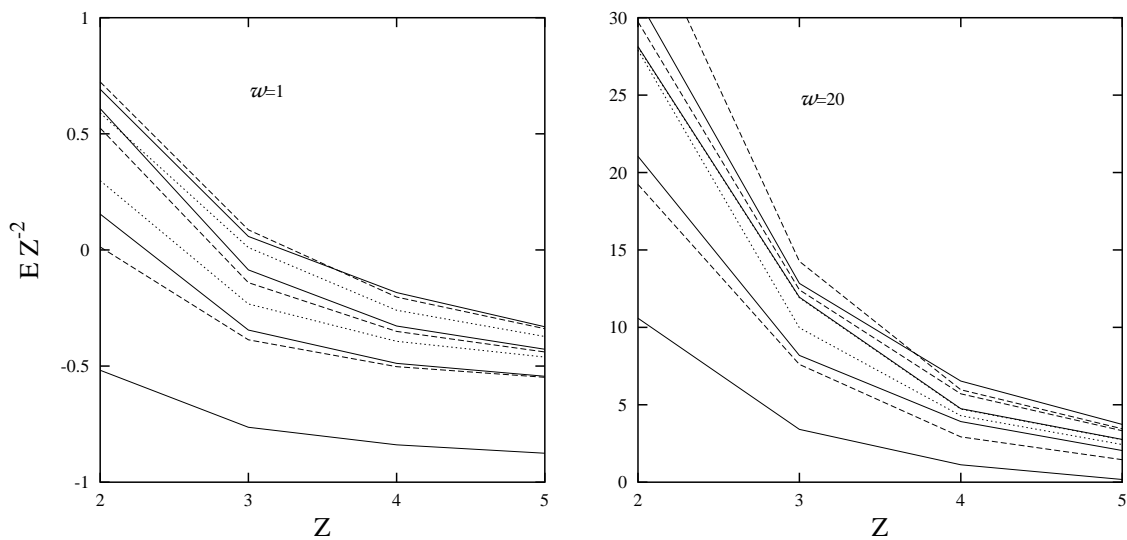
- For large  $Z$  the energy behaves like a quadratic function of  $Z$ .
- For small  $Z$  the linear and  $Z^{-1}$  terms dominate the energy expression.

The confinement does not change this general behaviour, though it may modify the energy level sequences.



$Z$ -dependence of energy levels  
in small  $Z$  systems (negative ions and quantum dots)  
for medium ( $\omega = 1$ ) and strong ( $\omega = 20$ )  
confinements

(All energies are in atomic units;  
Note difference in the energy scale in the two cases)



$Z$ -dependence of energy levels  
in large  $Z$  systems (positive ions)  
for medium ( $\omega = 1$ ) and strong ( $\omega = 20$ )  
confinements

(All energies are in atomic units;  
All energy levels are scaled by  $Z^{-2}$ ;  
Note the difference in the energy scale in the two cases)



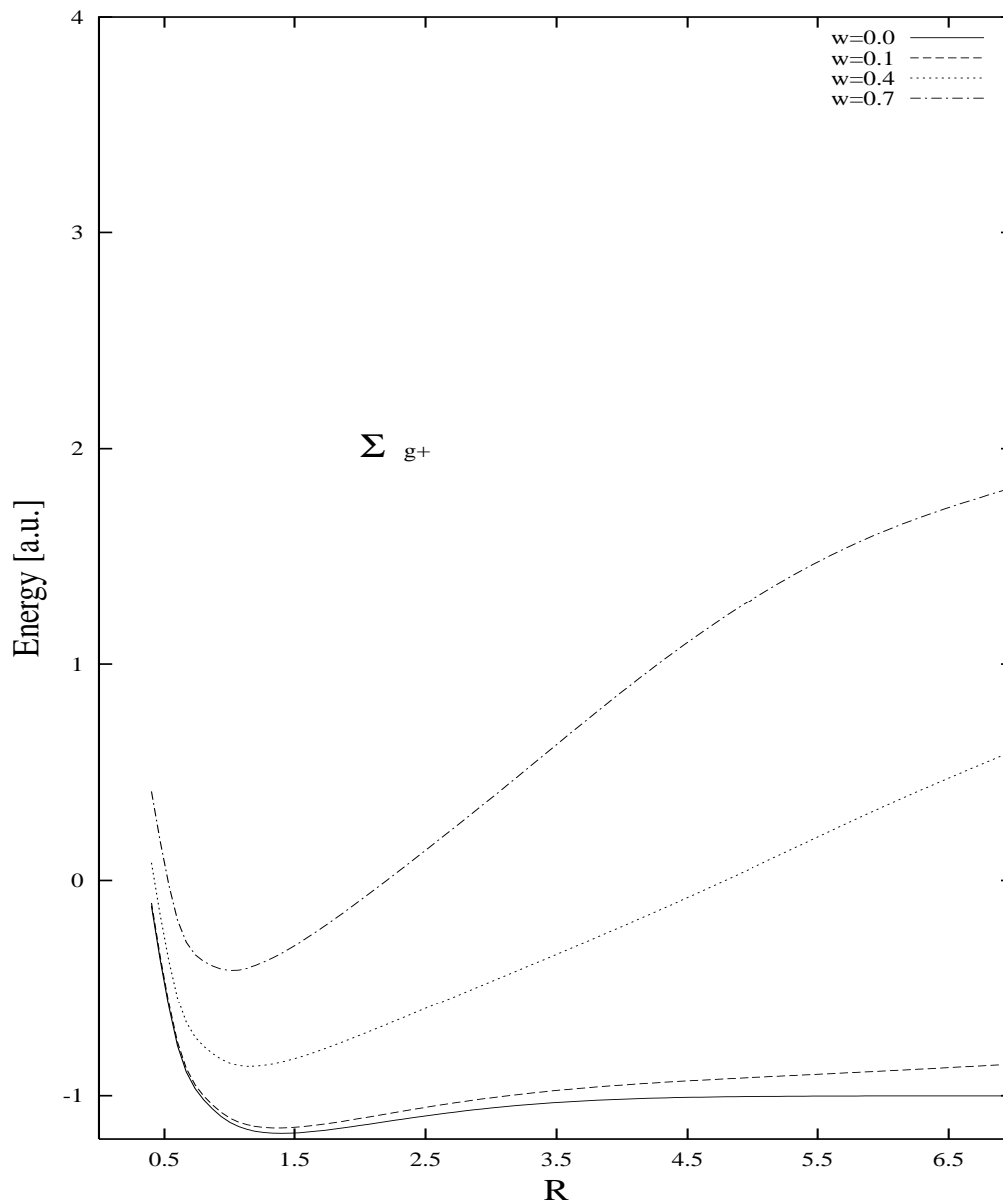
## Confinement of molecules

The confinement potential keeps the electronic charge in the middle of the cavity when the nuclei move apart. In consequence the binding of the molecule is increased by the confinement and increases with the strength of the confinement.

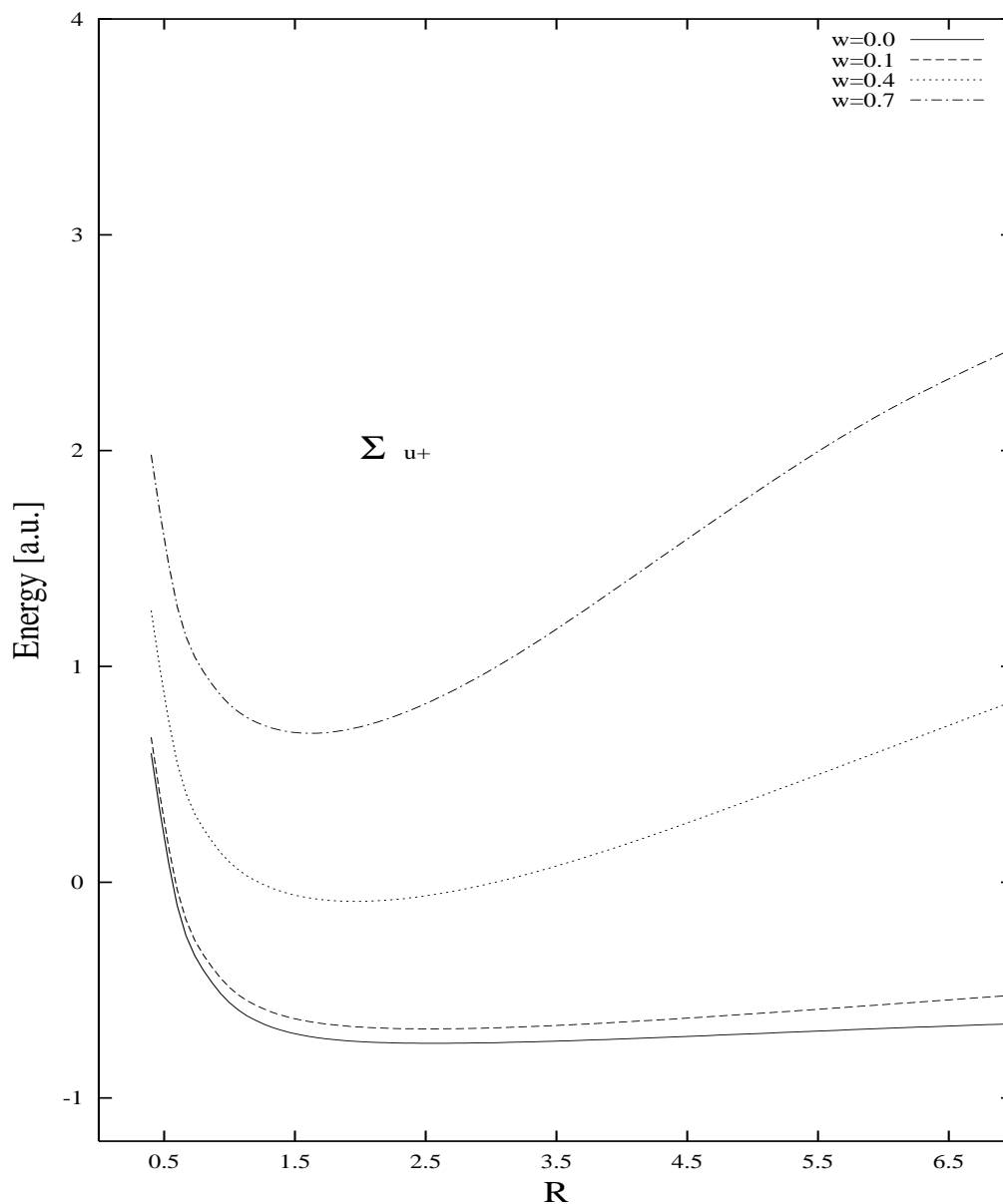
Consequently, due to the confinement:

- The vibrational levels are blue-shifted;
- The number of vibrational levels increases;
- The width of the ro-vibrational band becomes larger.





Potential energy curves  
for the ground state of  $H_2$  ( $X^1\Sigma_g^+$ )  
for different parameters  $\omega$ .



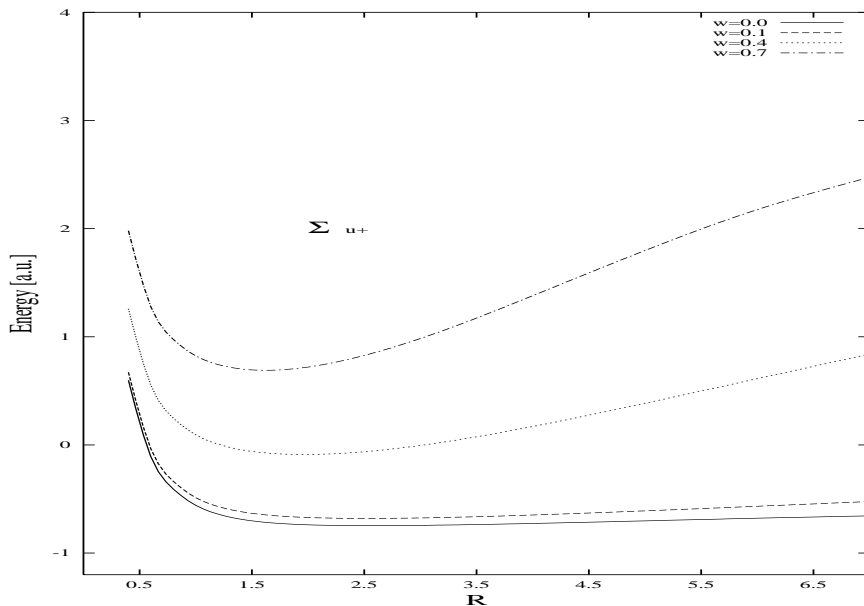
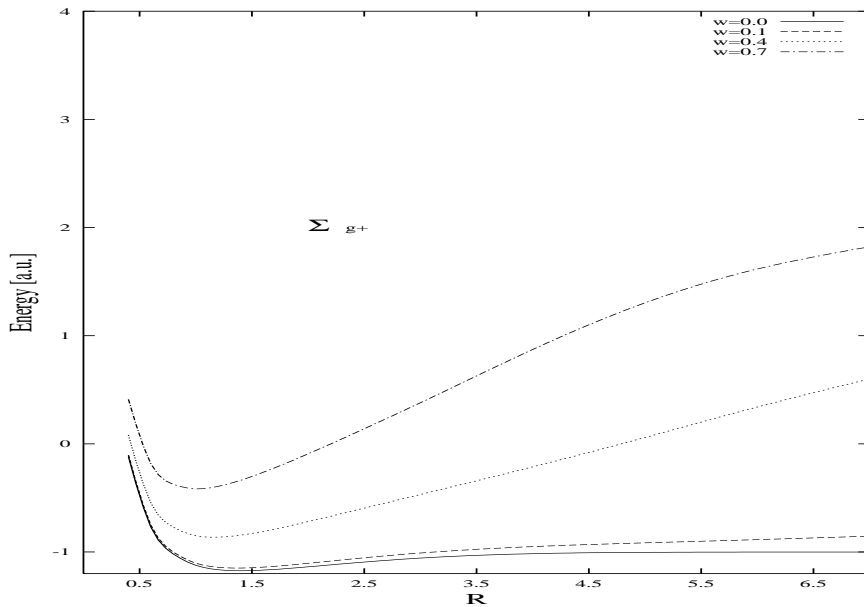
Potential energy curves  
for the first excited state of  $H_2$  ( $B^1\Sigma_u^+$ )  
for different parameters  $\omega$ .



H<sub>2</sub> molecule

$$V = 0.5w^{n+1}x^{2n} + 0.5w^{n+1}y^{2n} + 0.5w^{n+1}z^{2n}$$

n=1



Potential energy curves  
for the ground state of H<sub>2</sub> ( $X^1\Sigma_g^+$ ) and  
for the first excited state ( $B^1\Sigma_u^+$ )  
for different parameters  $\omega$ .



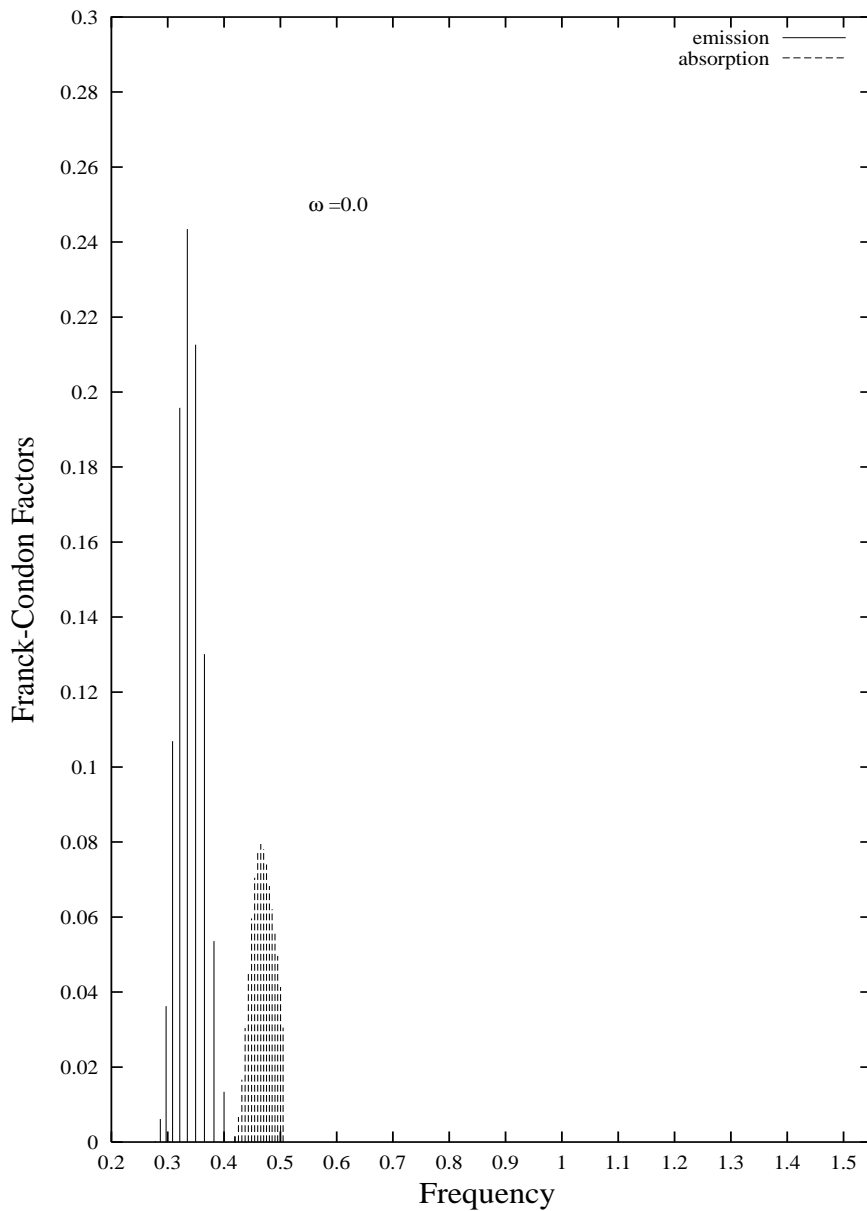
## Quality of the wavefunction and basis set

Internuclear equilibrium distance and zero-point vibrational energy in the  $^1\Sigma_g^+$  state of  $\text{H}_2$ :

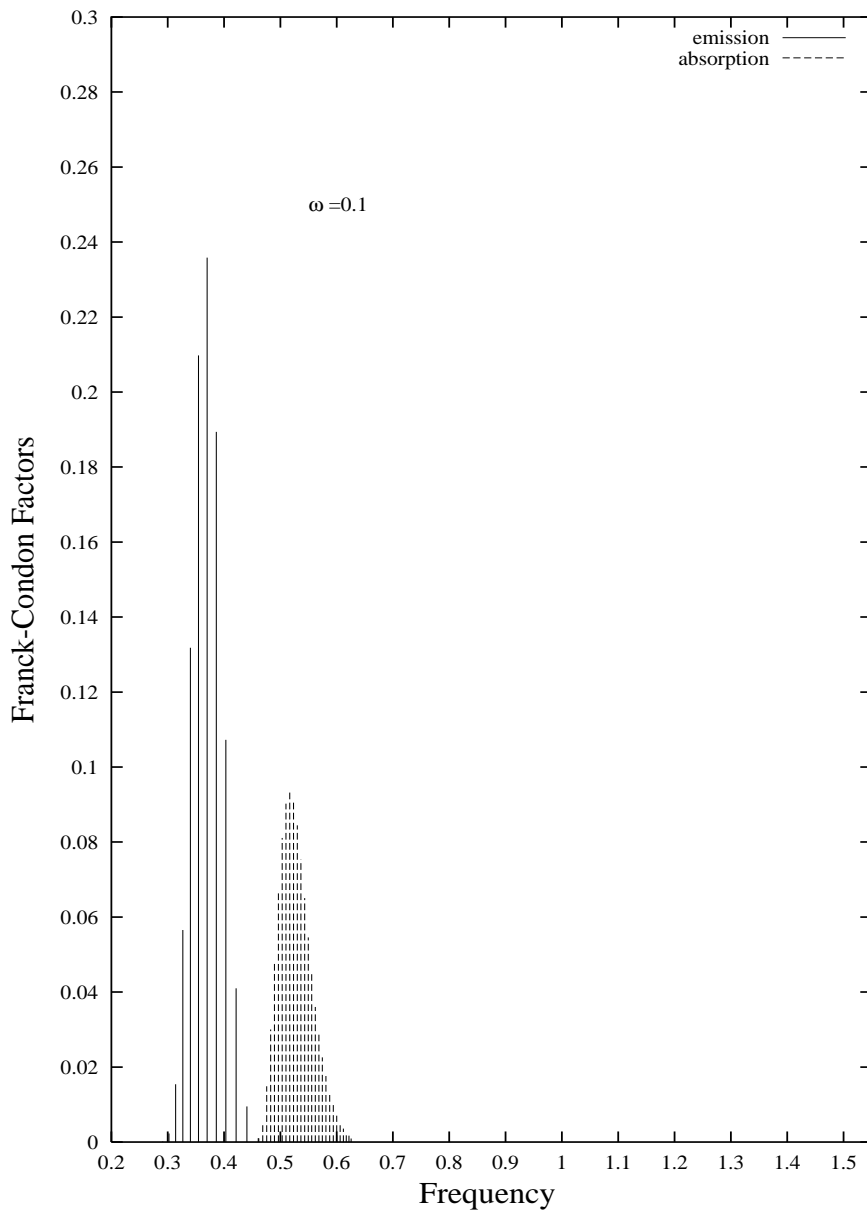
Case	$r_e/\text{\AA}$	$E_0^{vib}/\text{cm}^{-1}$
$\omega = 0.1$	0.7244	2270.57 <sup>a</sup>
$\omega = 0.0$	0.7405	2169.53 <sup>a</sup>
Experiment <sup>b</sup>	0.7414	2170.27

<sup>a</sup> calculated with LEVEL 7.1, R. LeRoy, Waterloo 2000

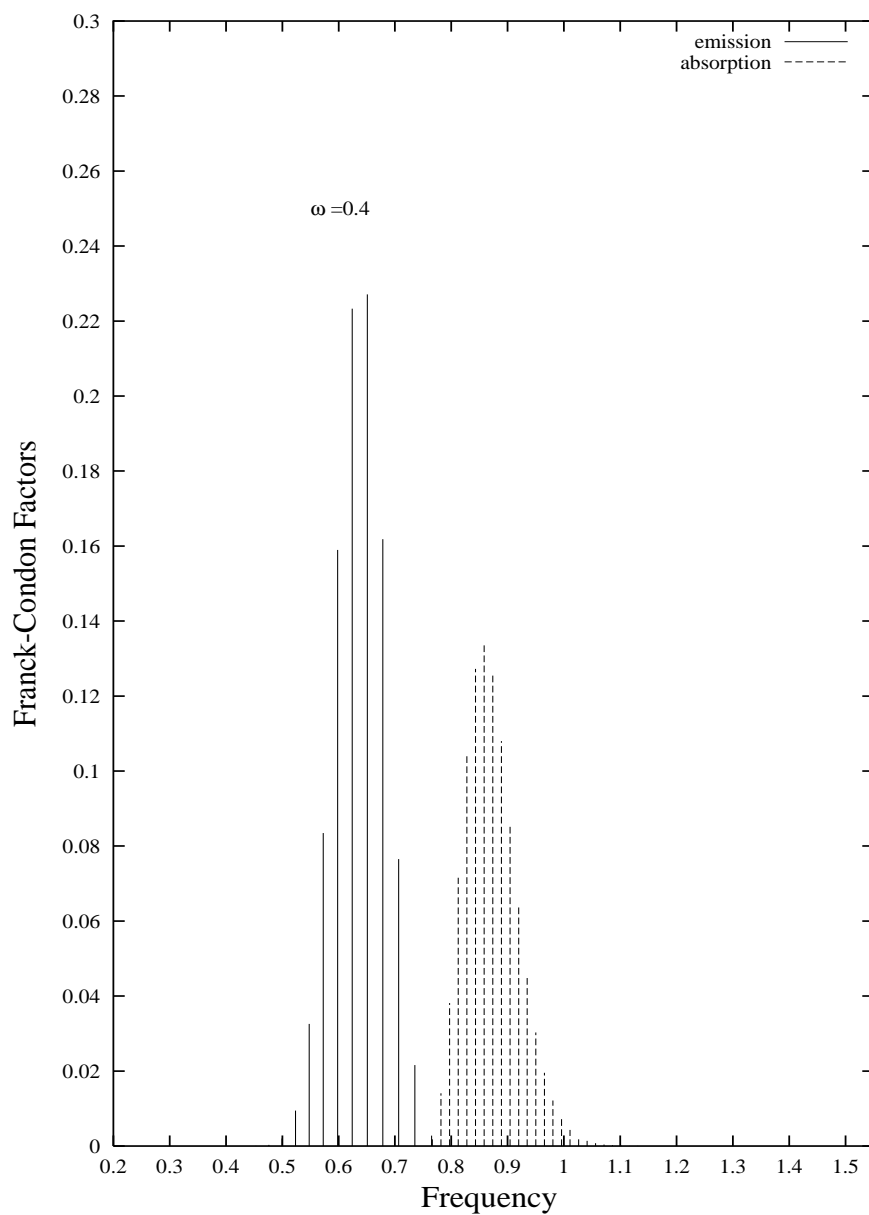
<sup>b</sup> K.P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. IV: Constants of Diatomic Molecules*, Van Nostrand, New York 1979



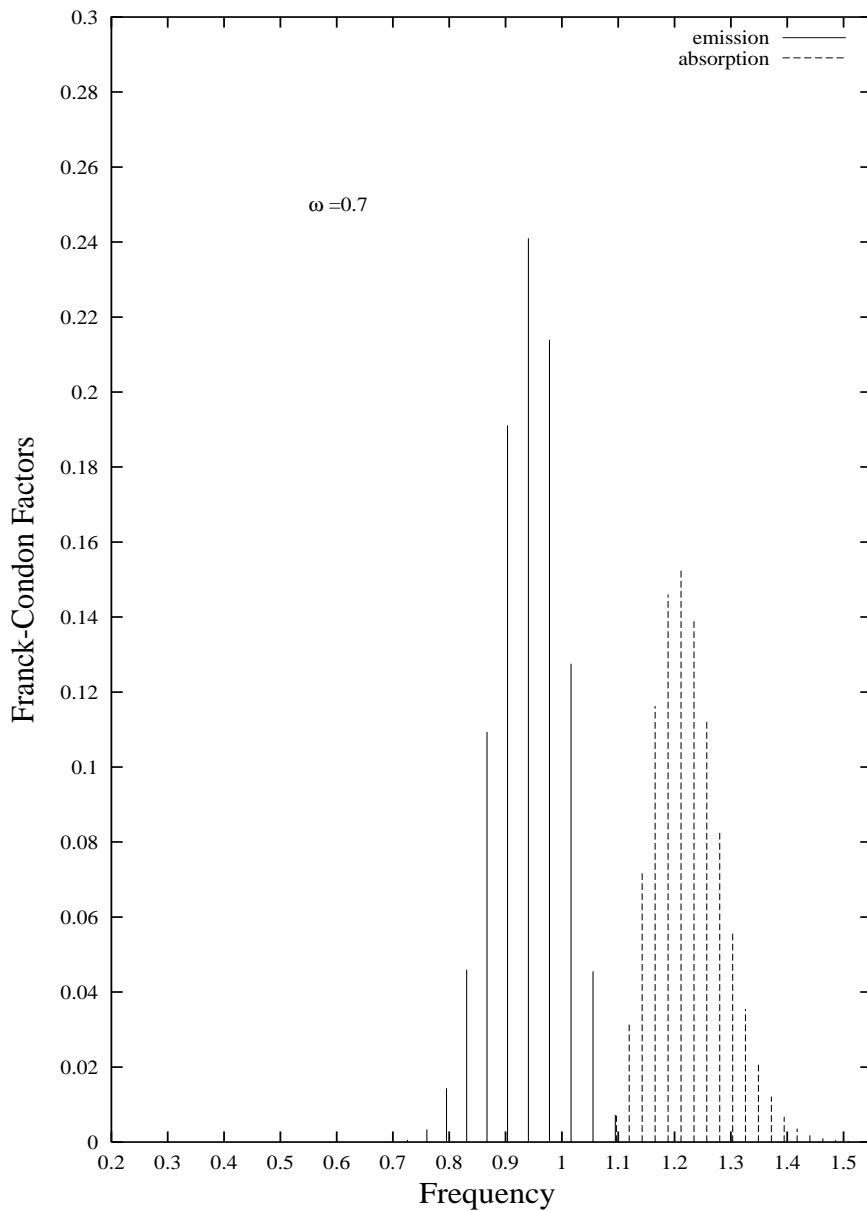
Franck-Condon Factors  
for  $X^1\Sigma_g + -B^1\Sigma_u +$  transitions  
in unconfined ( $\omega = 0.0$ )  $H_2$ .



Franck-Condon Factors  
for  $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$  transitions  
in confined ( $\omega = 0.1$ )  $H_2$ .

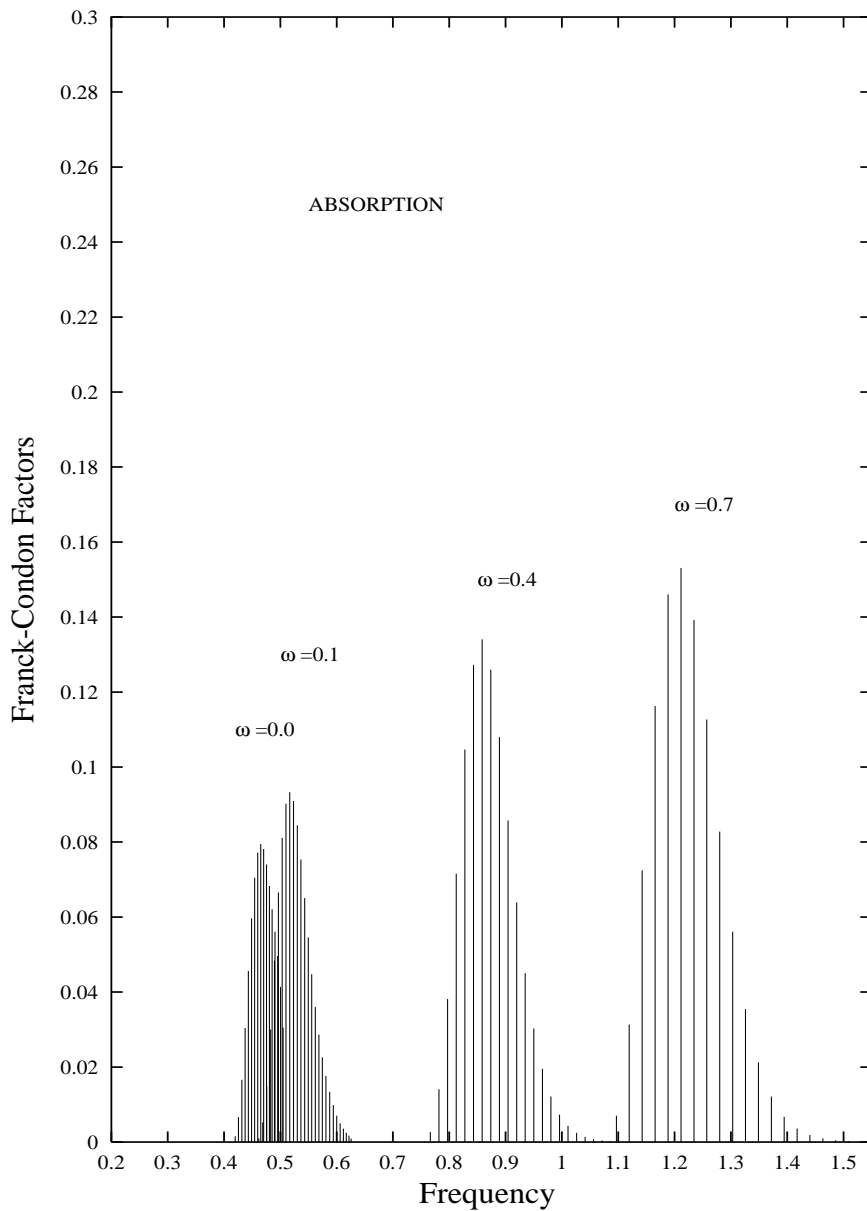


Franck-Condon Factors  
for  $X^1\Sigma_g + -B^1\Sigma_u +$  transitions  
in confined ( $\omega = 0.4$ )  $H_2$ .

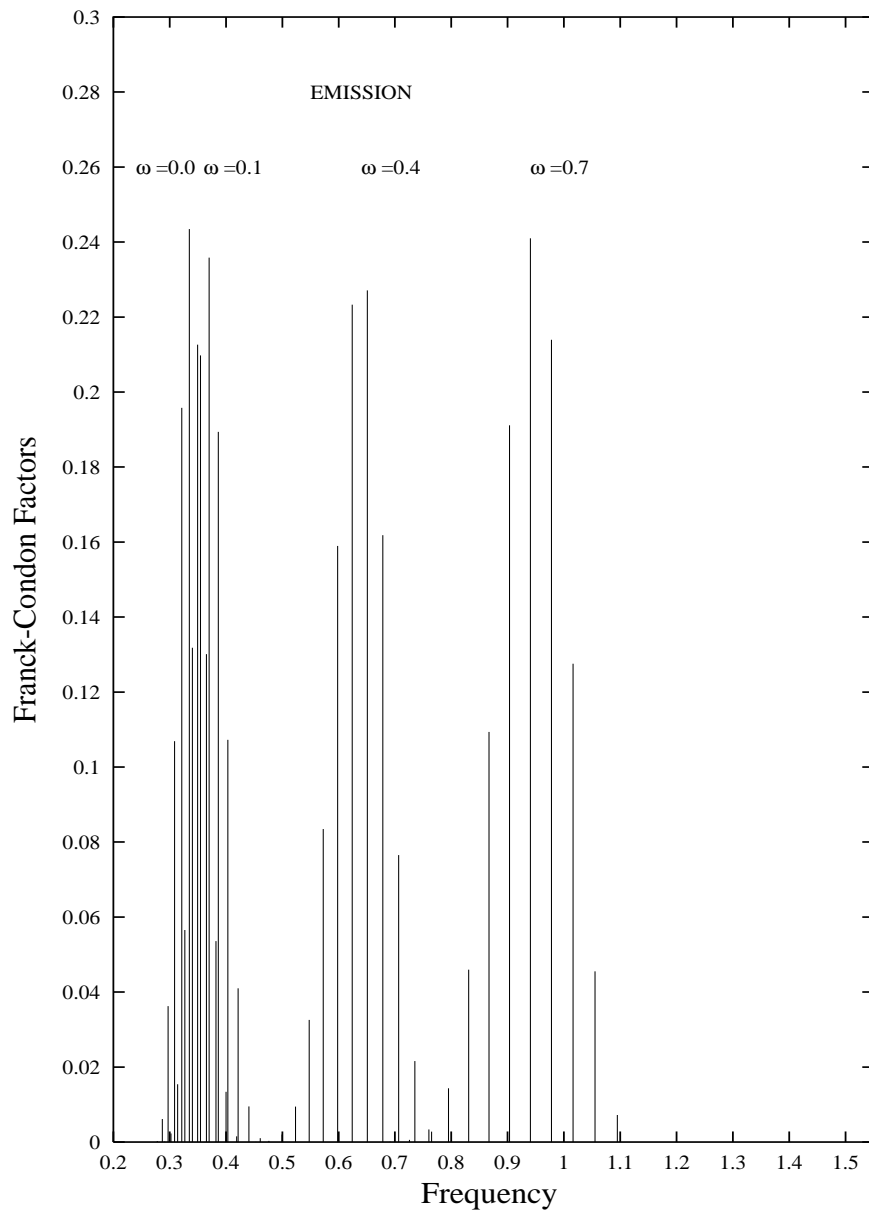


Franck-Condon Factors  
for  $X^1\Sigma_g + -B^1\Sigma_u +$  transitions  
in confined ( $\omega = 0.7$ )  $H_2$ .





Franck-Condon Factors  
for  $X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$  transitions in  $H_2$   
for different parameters  $\omega$ .



Franck-Condon Factors  
for  $B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$  transitions in  $H_2$   
for different parameters  $\omega$ .



## Next

- Studies of the properties of atoms on “muffin-tin”-type surfaces;
- Studies of the correlation between the surface shape and the spectral properties and reactivity of the confined atoms.
- Studies of the properties of molecules in nanocavities and in nano-tubes;
- Studies of the correlation between the shape of the confining potential and the properties of the confined systems;
- Studies of the shape of confinements which would produce quantum systems with assumed properties.