ab-initio calculation of structural properties of cubic ice

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Outline

1-Different phases of ice

2-Theoretical aspect of the work

3- Data analysis

4- Conclusions

The most important matter in the world is water. 15% of the weight of Earth is water , and in the North and South ocean most of them is in the form of ice. Therefore physical and chemical properties, of different phases of ice are great important.

Diagram of various phases of ice

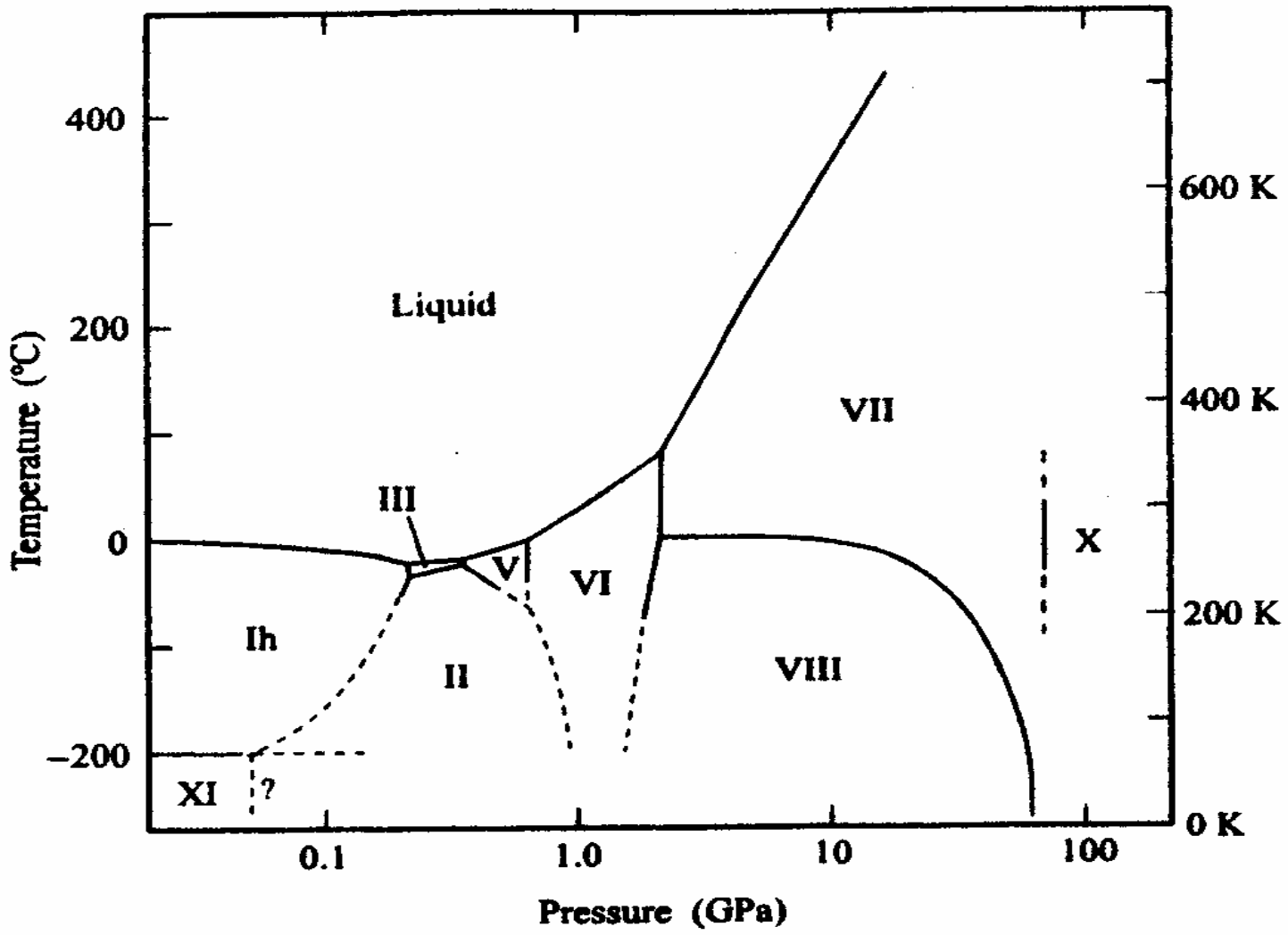
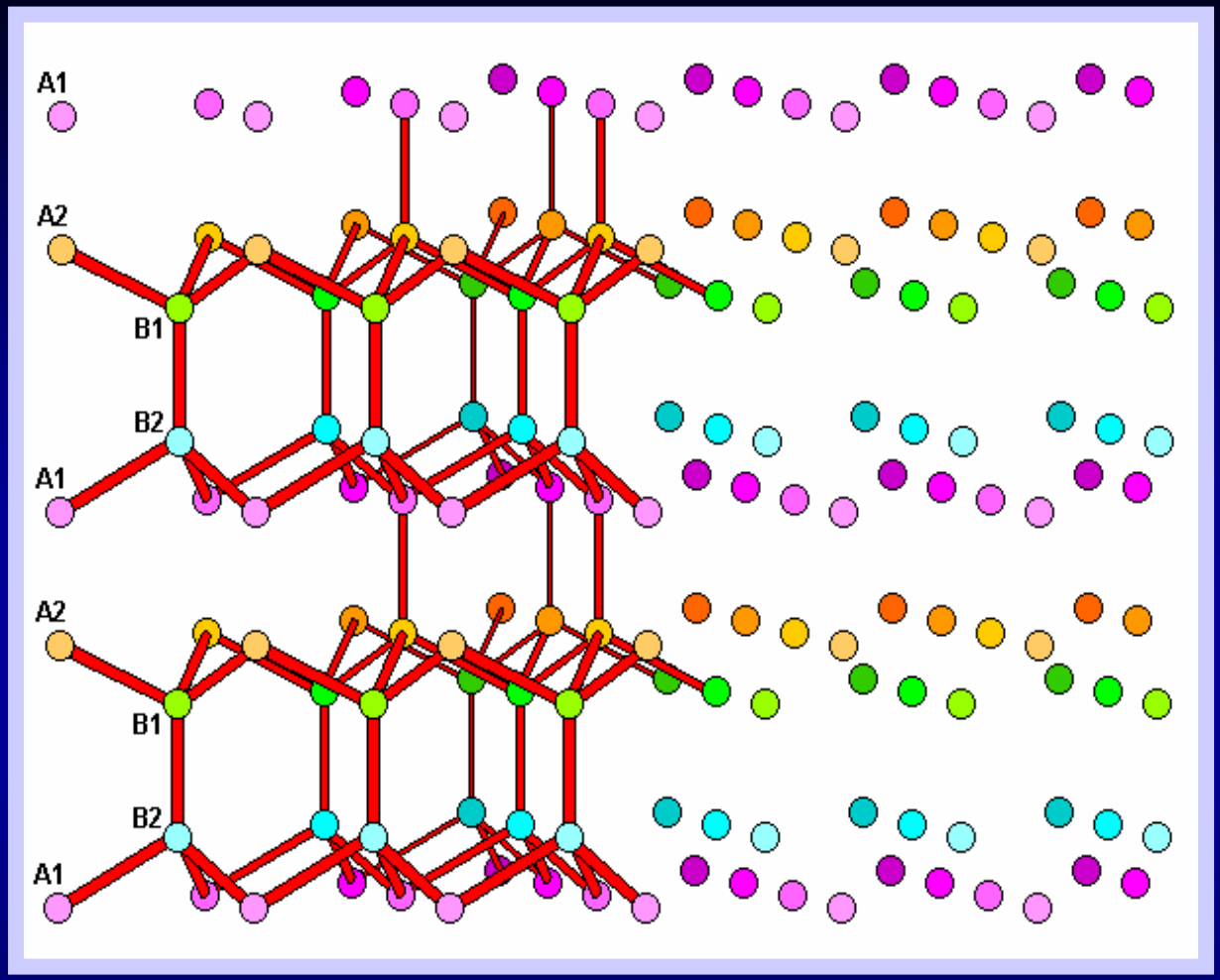


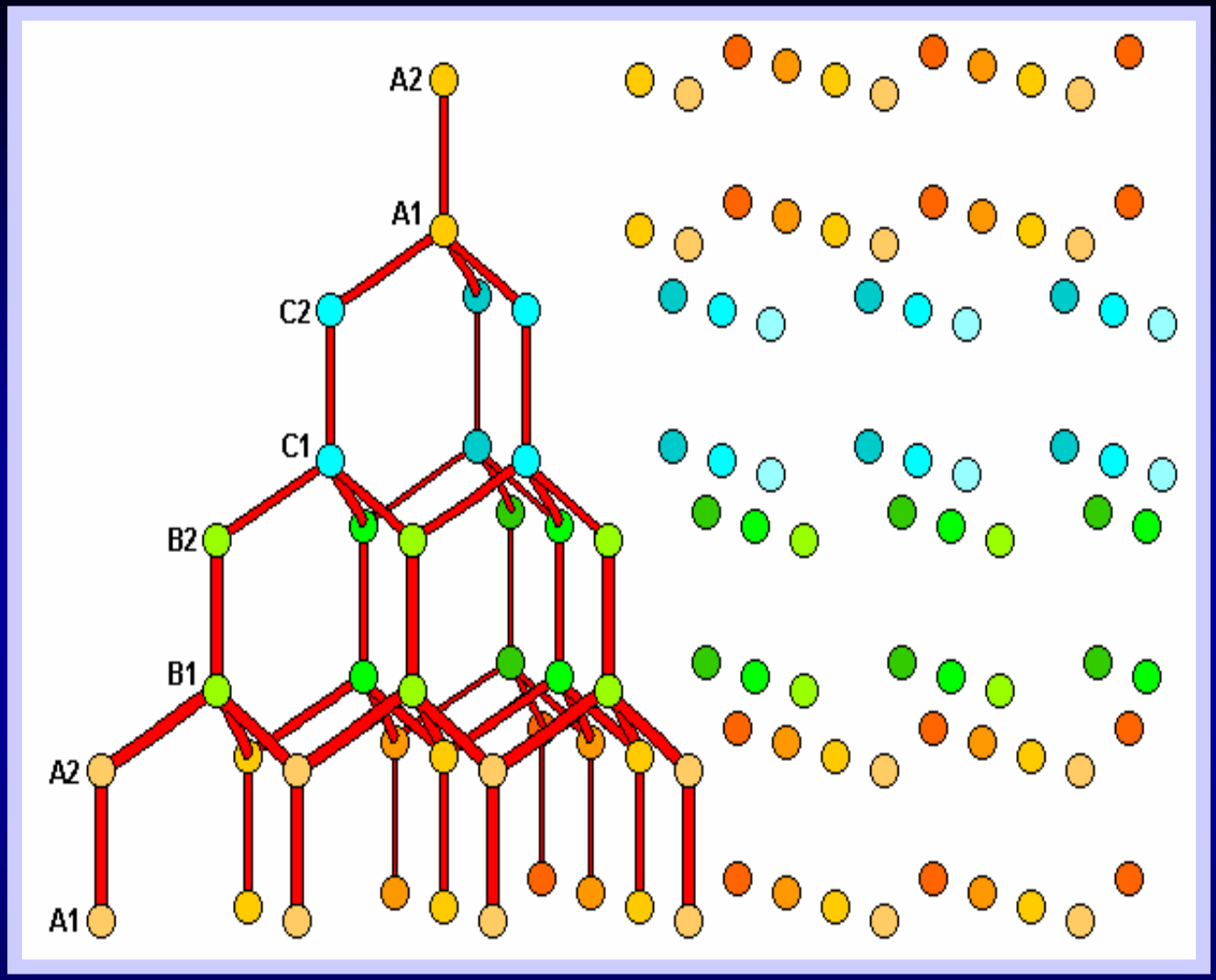
Table of different phases of ice with their relative parameters

Ice	Crystal system	Space group	Proton order?	Molecules per cell	T (K)	p (GPa)	Density (Mg m^{-3})	Cell parameters (Å)	Reference
Ih	Hex.	$P6_3/mmc$	N	4	250	0	0.920	$a = 4.518$, $c = 7.356$	Röttger *et al.* (1994)
Ic	Cubic	$Fd\bar{3}m$	N	8	78	0	0.931	$a = 6.358$	Kuhs *et al.* (1987)
II	Rhomb.	$R\bar{3}$	Y	12	123	0†	1.170	$a = 7.78$, $\alpha = 113.1°$	Kamb (1964)
III	Tetrag.	$P4_12_12$	N	12	250	0.28	1.165	$a = 6.666$, $c = 6.936$	Londono *et al.* (1993)
IV	Rhomb.	$R\bar{3}c$	N	16	110	0†	1.272	$a = 7.60$, $\alpha = 70.1°$	Engelhardt and Kamb (1981)
					260	0.50	1.292		Lobban *et al.* (1998)
V	Monocl.	$A2/a$	N	28	98	0†	1.231	$a = 9.22$, $b = 7.54$, $c = 10.35$, $\beta = 109.2°$	Kamb *et al.* (1967)
					223	0.53	1.283		Kamb *et al.* (1967)
VI	Tetrag.	$P4_2/nmc$	N	10	225	1.1	1.373	$a = 6.181$, $c = 5.698$	Kuhs *et al.* (1984)
VII	Cubic	$Pn\bar{3}m$	N	2	295	2.4	1.599	$a = 3.344$	Kuhs *et al.* (1984)
VIII	Tetrag.	$I4_1/amd$	Y	8	10	2.4	1.628	$a = 4.656$, $c = 6.775$	Kuhs *et al.* (1984)
IX	Tetrag.	$P4_12_12$	Y	12	165	0.28	1.194	$a = 6.692$, $c = 6.715$	Londono *et al.* (1993)
X	Cubic	$Pn\bar{3}m$	n.a.	2	300	62	2.79	$a = 2.78$	Hemley *et al.* (1987)
XI	Ortho.	$Cmc2_1$	Y	8	5	0	0.934	$a = 4.465$, $b = 7.858$, $c = 7.292$	Line and Whitworth (1996)
XII	Tetrag.	$I\bar{4}2d$	N	12	260	0.50	1.292	$a = 8.304$, $c = 4.024$	Lobban *et al.* (1998)

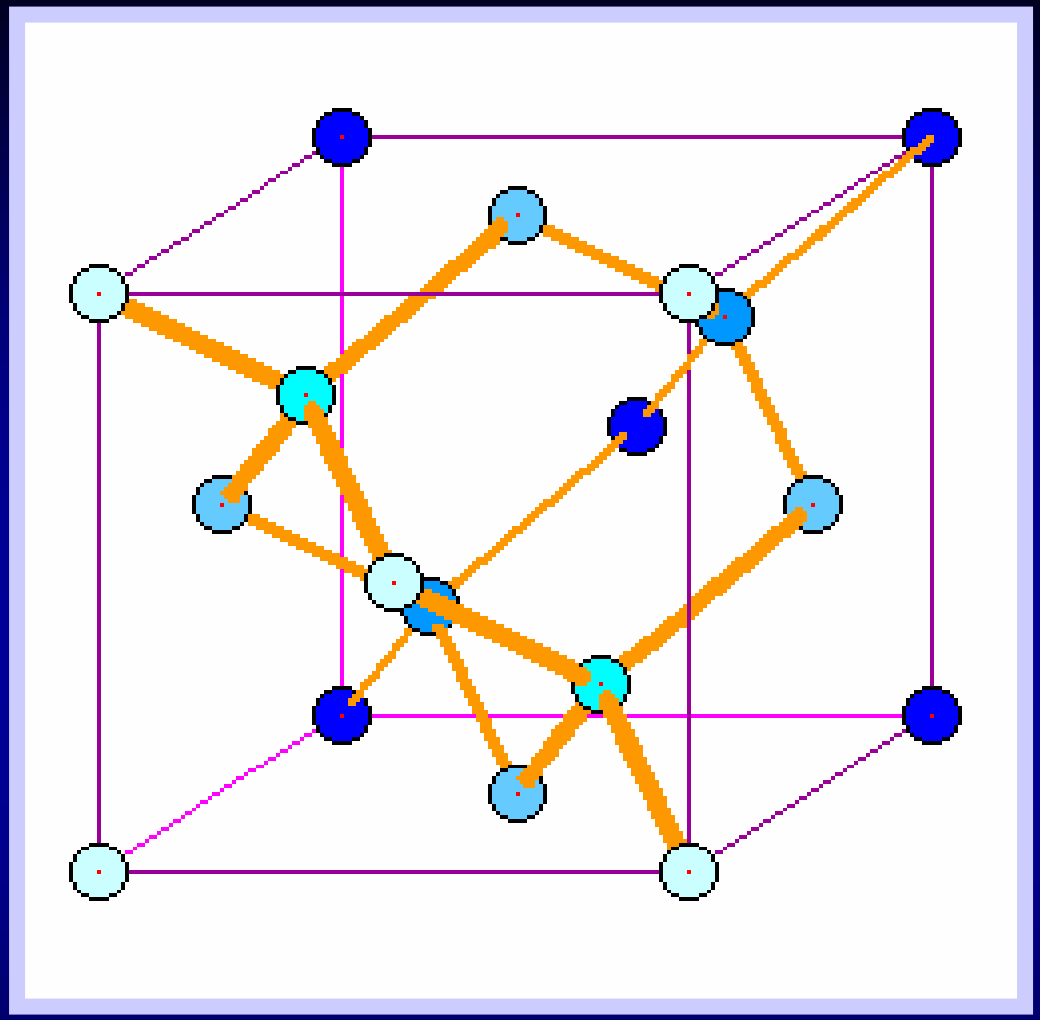
† Samples recovered at low temperature.



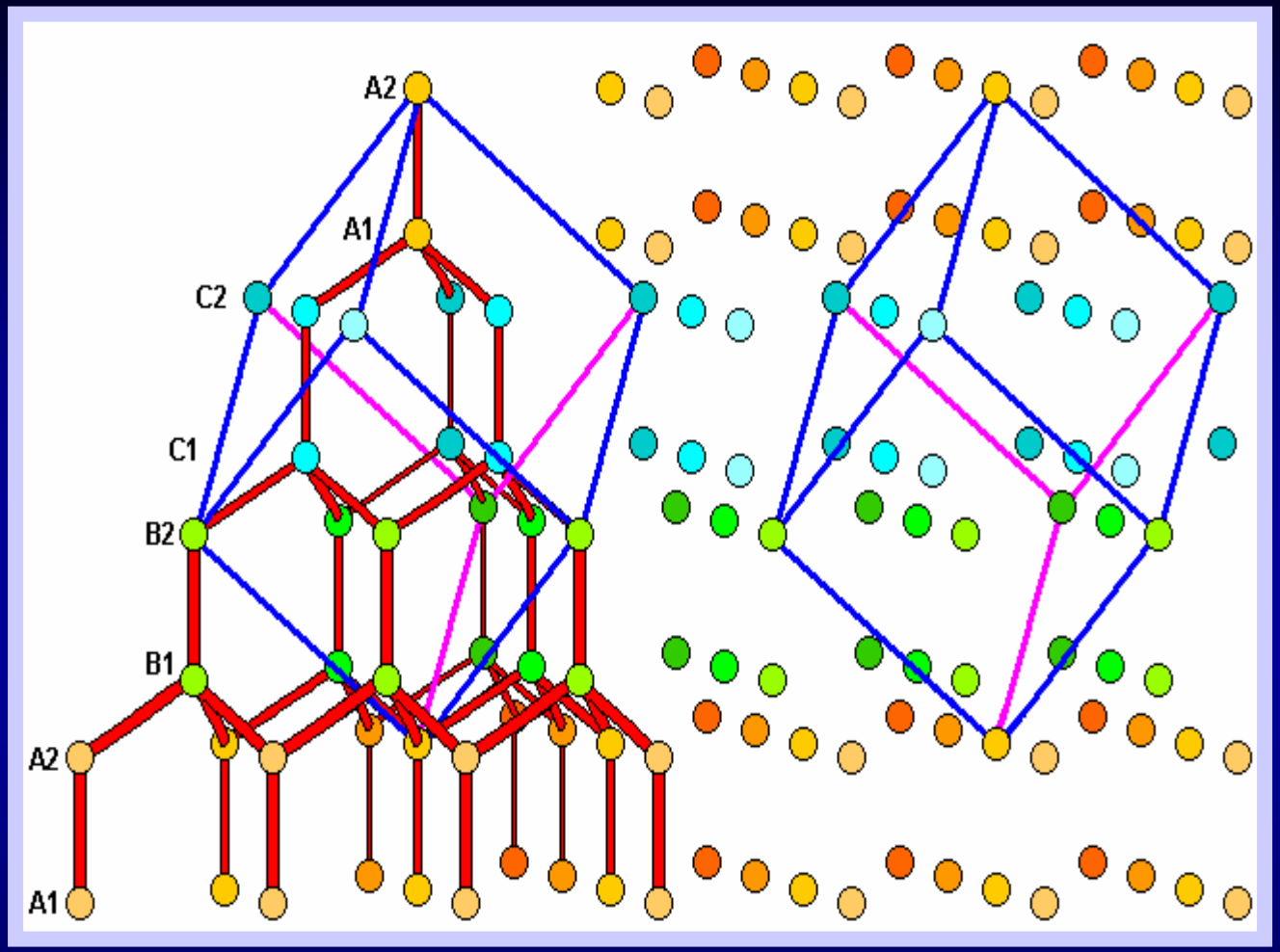
General ice with hexagonal structure (IceIh) between -80 up to 0 centigrade and general pressure



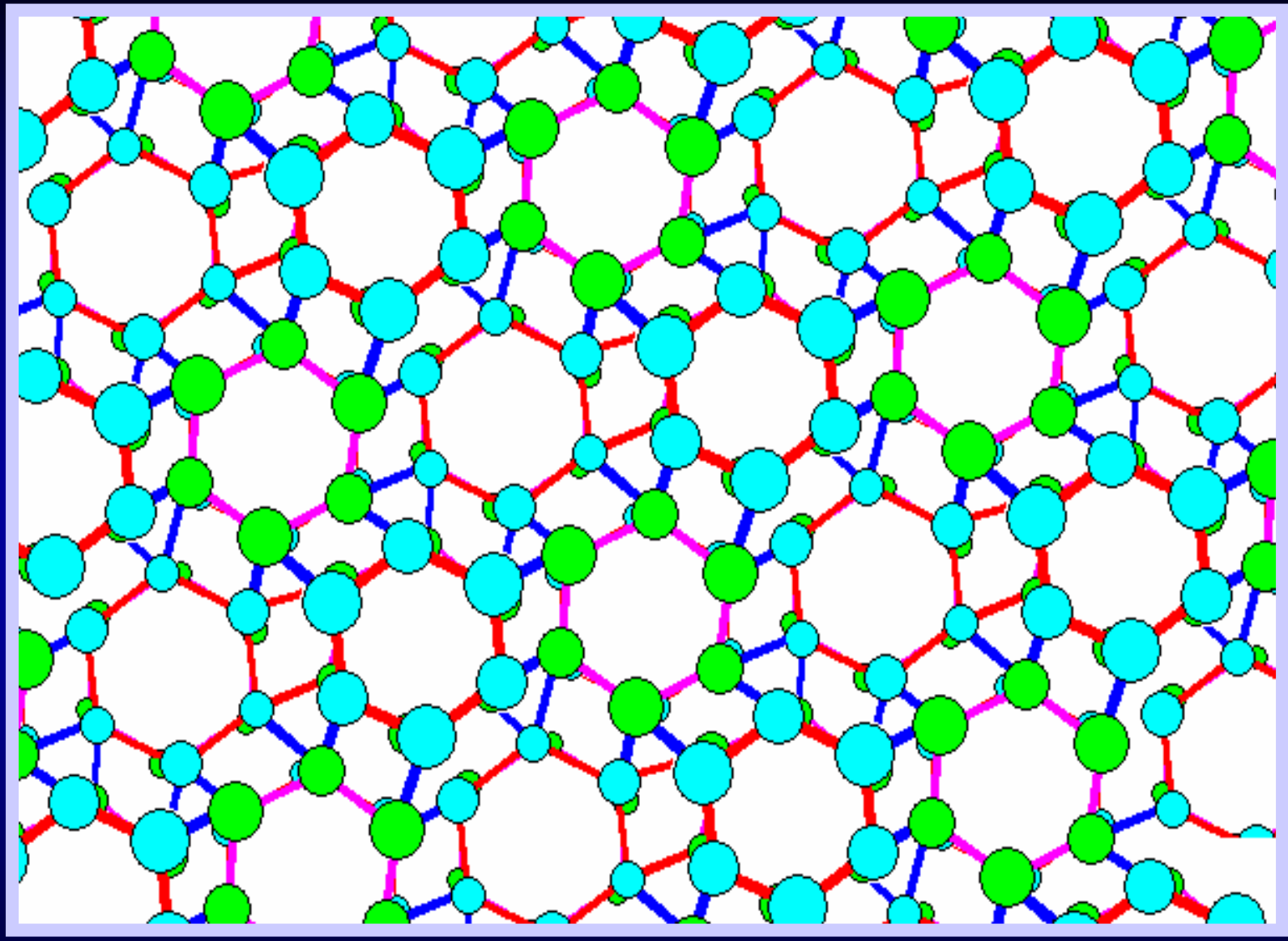
Structure of cubic ice between -130 up to -80 centigrade which is unstable . This phase can be produced from phases II ,III ,VI,VII in liquid nitrogen temperature. In -100Ċ the cubic ice changes to Ih phase of ice.



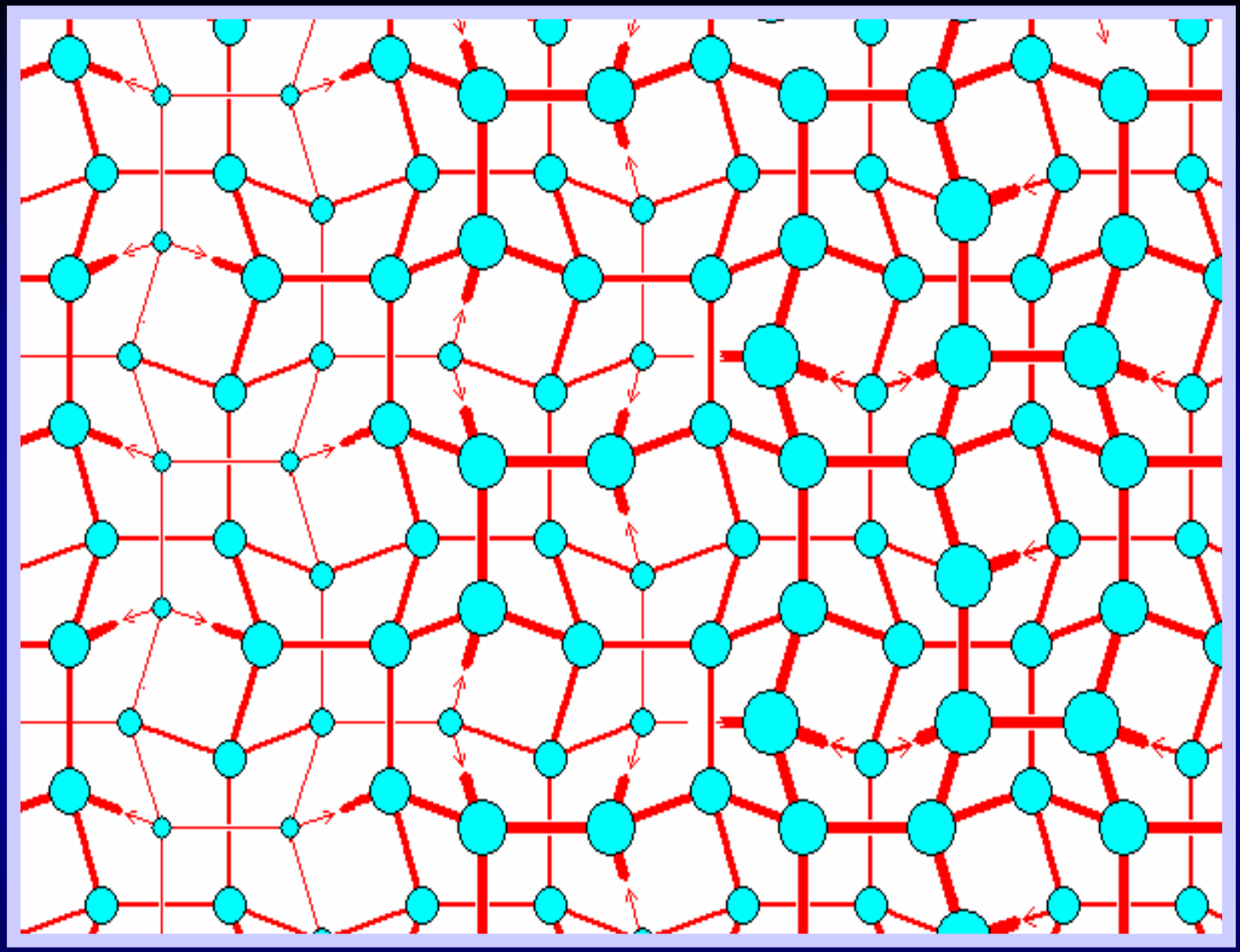
Unit cell of cubic ice which shows only oxygen atoms . O-H-O bands are represented with orange lines



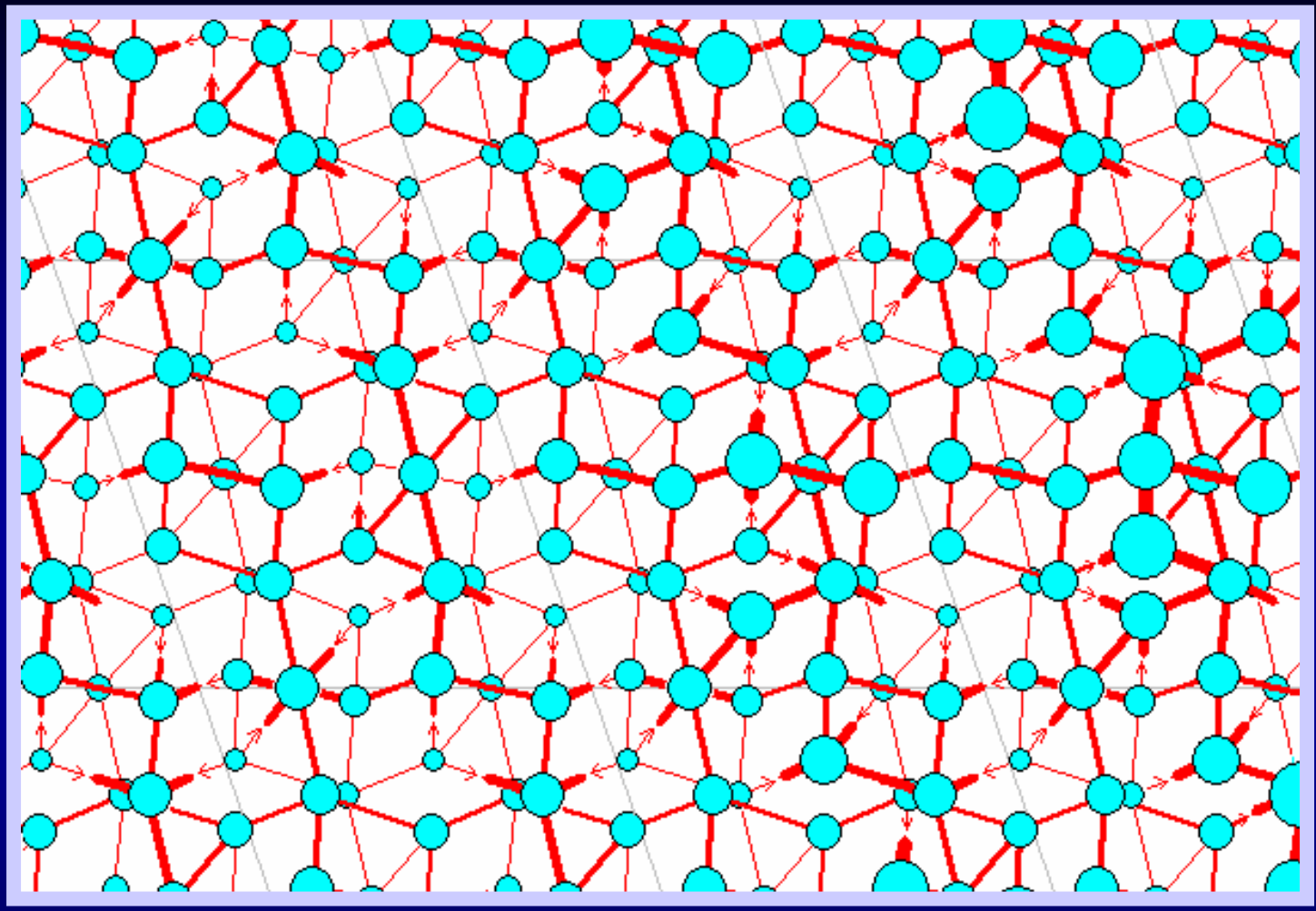
Relation between unit cell and layer structure in closed-packed of cubic ice



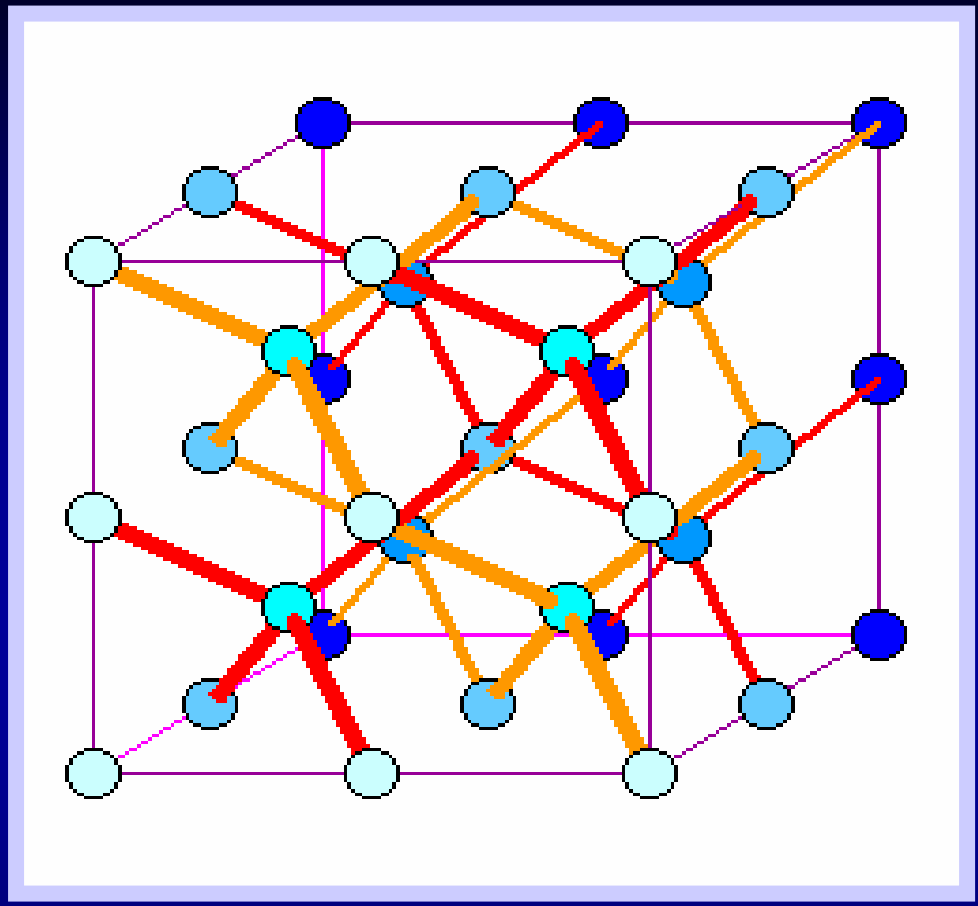
Ice- II phase with rhombohedral structure



Cubic III-phase structure, oxygen atoms shows with blue circle which closer oxygen with bigger circle and O-H-O bands represented as red lines



Cubic V-phase with monoclinic structure. The unit cells are represented as cubic



Cubic VII phase composes of two structures of cubic Ice which represented one with red lines and the other with orange lines. The conventional cell has 8 bcc cubic.

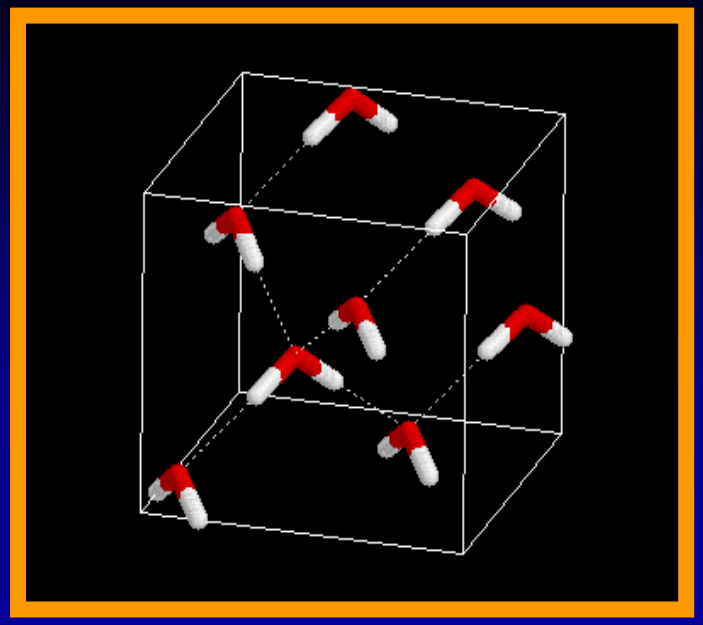
Cubic Ice

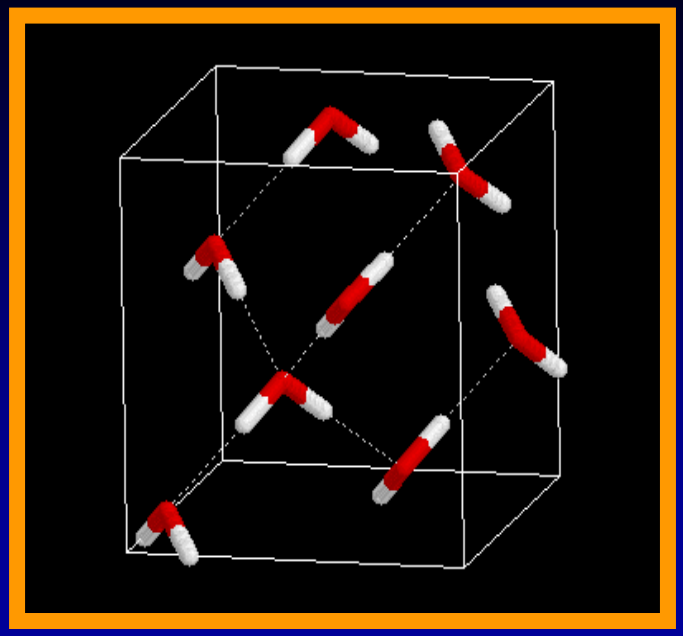
In this structure eight molecules of water are in the conventional cell. Number of configurations are 2**16.Bernell-Fowler rules are restricted the number of states.

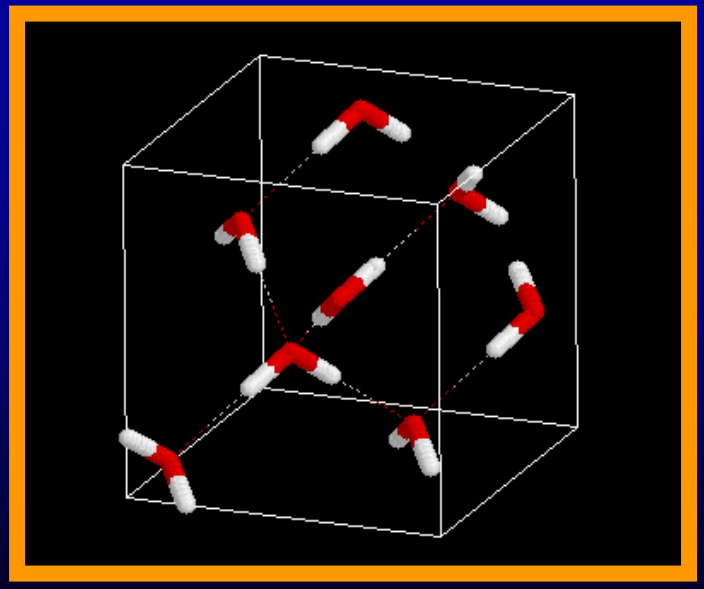
1) The distance between each oxygen and hydrogen atoms in a molecule is about 0.95 angstrom.

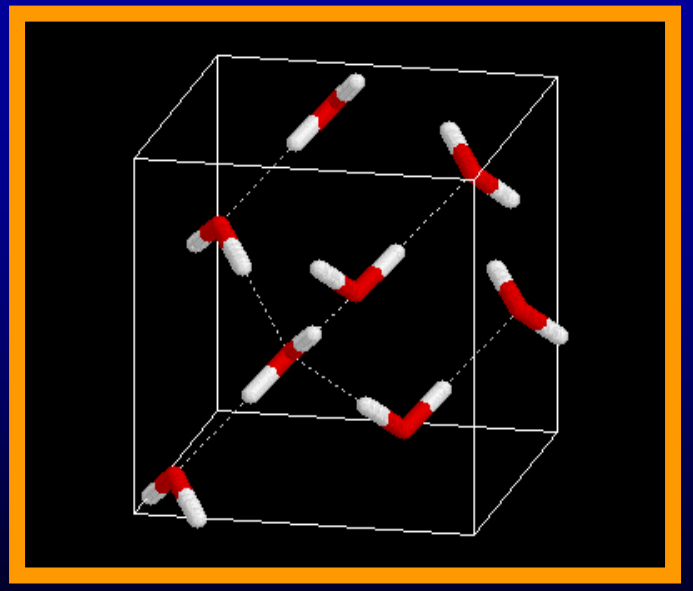
2) Water molecule in unite cell stay in a position where only one hydrogen of each molecule is located between two oxygen atoms.

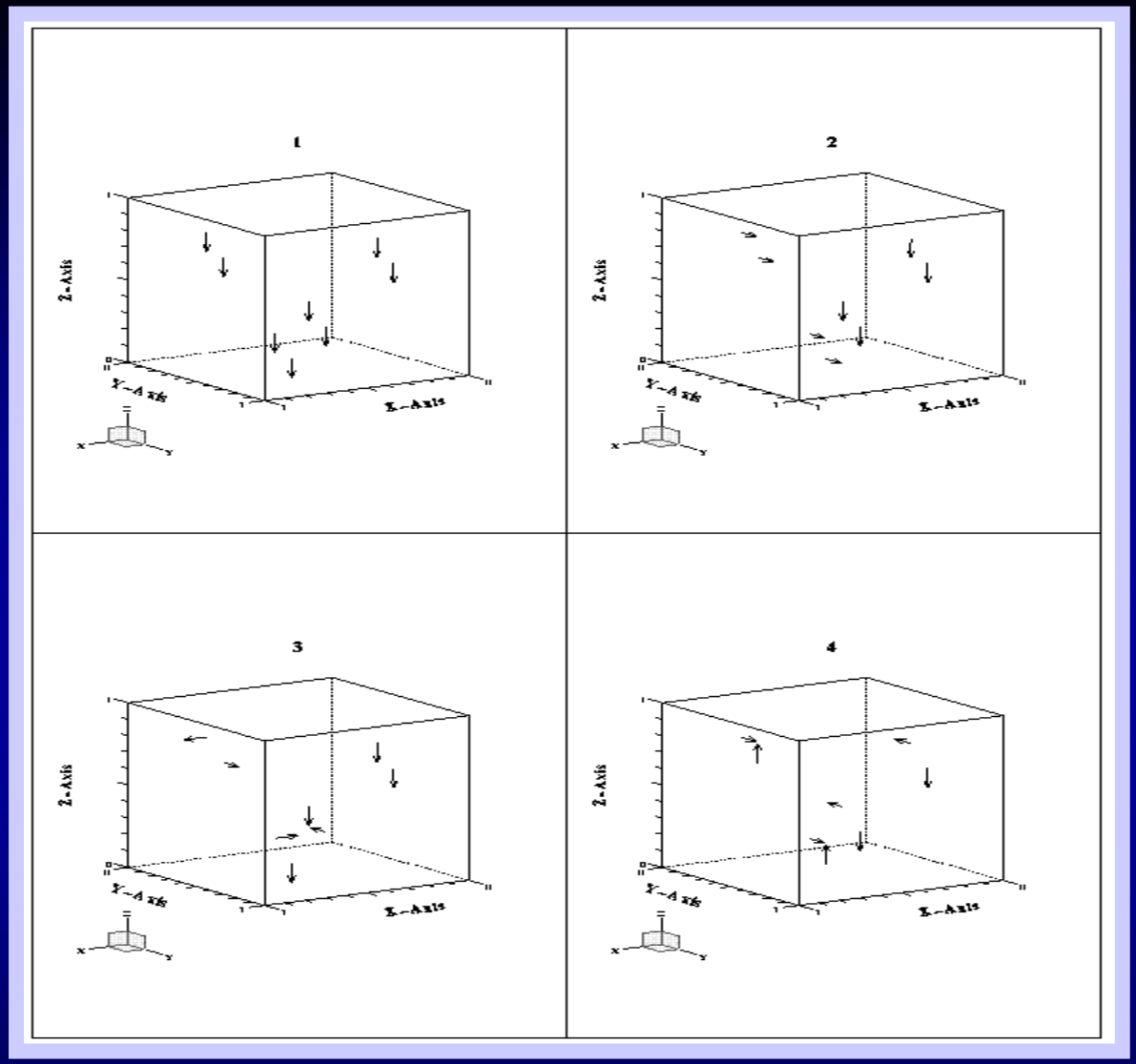
3) Each molecule of water has surrounded by for other oxygen atoms. It is located somehow that always two hydrogen atoms pointed to two oxygen atoms.











Total dipole moments of each configurations of cubic ice structures which are 8,4√2,4 and 0 respectively.

The important of computational physics in solid state physics

1- Analysis of physical phenomena which are not possible to happen or if they happen, it is not possible to repeat them.
2-Variation of parameters in a physical process in the direction and size of variation which are not normal.

3-Many body system → Classic
3-Many body system → Quantum

Born-Oppenhimer approximation

Nucleus in atoms are stable regarding to the motion of electrons

$$H\psi(\vec{r}_1,\vec{r}_2,\ldots\vec{r}_N,R_1,R_2,\ldots R_\alpha)=E\psi(\vec{r}_1,\vec{r}_2,\ldots\vec{r}_N,R_1,R_2,\ldots,R_\alpha)$$

$$H = H_k^e + H_k^N + H^{e-N} + H^{e-e} + H^{N-N}$$

$$(H_k^e + H_e + H^{e-e})\psi(r_i) = E_e\psi(r_i)$$

$$(H_k^N + H_e + H^{N-N})\psi(R_\alpha) = E_{total}\psi(R_\alpha)$$

$$E_{tot} = E_e + E_{nn}$$

Solution of Schrodinger equation for system of electrons

First we have to change equation of system of electrons to a sum of separate equations for each electron. There are two approaches for it:

1- Wave function is accepted as a variable parameter: Hartree and Hartree-Fock methods.

2- Density is considered as a variable parameter : Tomas Fermi and density functional theory

Hartree and Hartlee-Fock method:

In this method the wave function of the system is considered as a multiplication of wave functions of single particles. Also we consider that each electron see an effective potential from nucleus and other electrons

$$\psi(\vec{r}_1, \vec{r}_2, ..., \vec{r}_3) = \psi(\vec{r}_1)\psi(\vec{r}_2)...\psi(\vec{r}_N)$$

$$(\frac{-\hbar^2}{2m}\nabla^2 + V_{ext})\psi_i(\vec{r}_i) = \varepsilon_i\psi_i(\vec{r}_i)$$

$$V_{ext}(r) = -e^2\sum_{\alpha}\frac{Z_\alpha}{|\vec{r}_i - \vec{r}_\alpha|} + e\int\frac{dr' n(\vec{r}')}{|\vec{r} - \vec{r}'|}$$

$$n(\vec{r}) = \sum_i |\psi_i(\vec{r}_i)|^2$$

Density functional theory

This theory in 1964 presented by Kohn and Hohonberg.We can deduced all properties of a system in ground state using density of ground state.

$$E[n(\vec{r})]=T[n(\vec{r})]+\int n(\vec{r})V(\vec{r})dr+\frac{e^2}{2}\iint drdr'\frac{n(\vec{r})n(\vec{r})}{|\vec{r}-\vec{r}|}+E_{XC}[n(\vec{r})]$$

Kohn and Sham in 1965 replace the equation of the system by groups of equations of single particles in the system.

Problems with single particle equations

Very large number of electrons in system:

Using Bloch theorem and choosing appropriate K in reciprocal lattice.

Wave function of a particle in level n with wave vector of K

$$\psi_{n,\vec{K}}(\vec{r}) = \exp(i\vec{K}.\vec{r})u_{n,\vec{K}}(\vec{r})$$

$$u_{n,\vec{K}}(\vec{r}) = u_{n,\vec{K}}(\vec{r}+\vec{R})$$

$$u_{n,\vec{K}}(\vec{r}) = \sum_{\vec{G}'} c_n(\vec{K}+\vec{G})\exp(i\vec{G}.\vec{r})$$

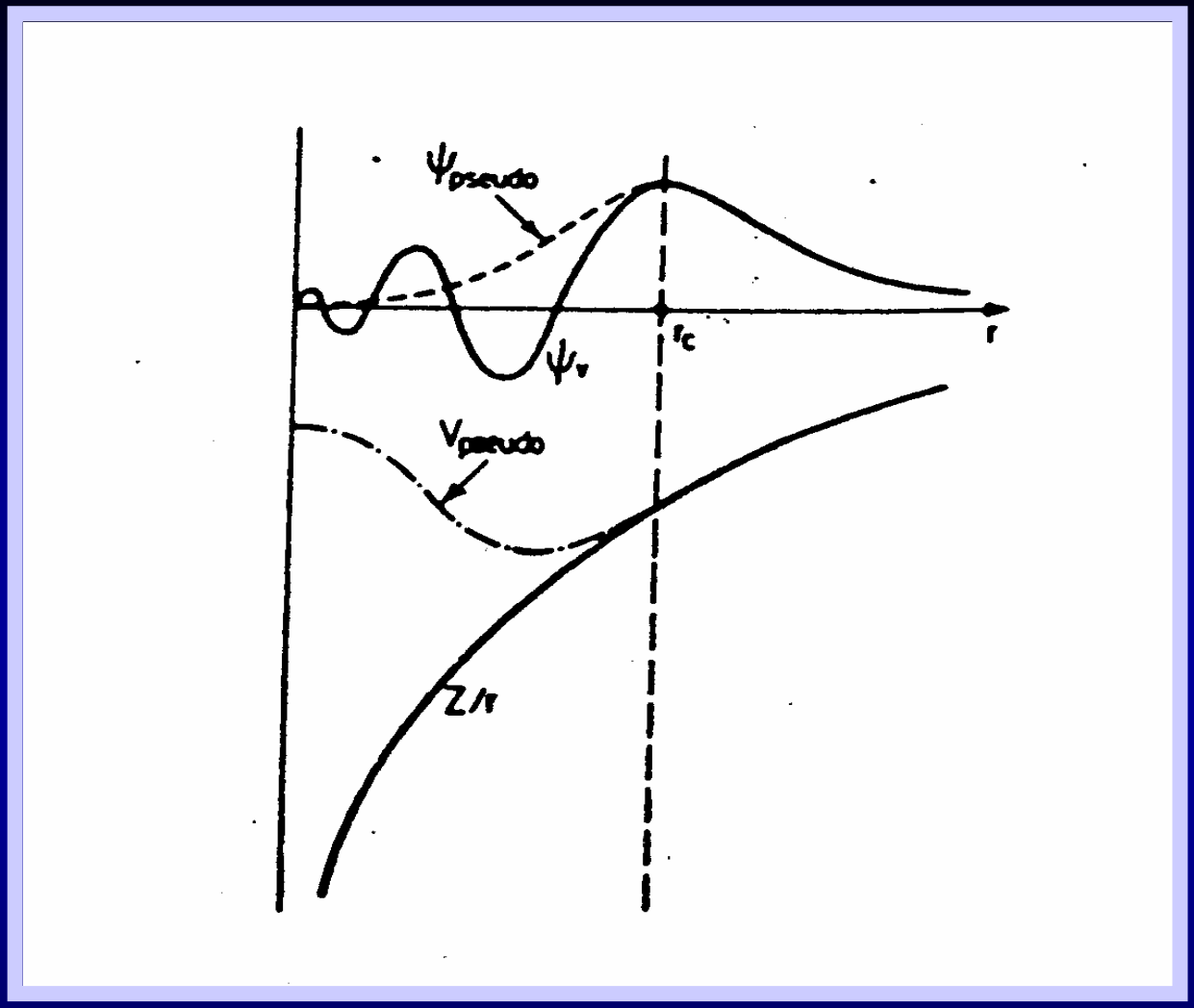
$$\psi_{n,k}(\vec{r}) = \sum_{\vec{G}'} c_n(\vec{K}+\vec{G})\exp[i(\vec{K}+\vec{G}).\vec{r})]$$

Pseudo potential approximation

- Area around the nucleus is divided to core and valance regions

- Wave function of core electrons are localized in the region and play no role in ionic bonds.

- Valance electrons in core region have high kinetic energy and their wave function has a lot of vibrations in the core which need a huge number of plane wave for their construction.
- In summation plane wave those with low kinetic energy has more important. Therefore we can continue the extension of plane waves up to a certain value called **cut off energy.**



Wave function,pseudo wave function, real potential and pseudo potential are illustrated qualitatively

Properties of ad-initio pseudo potentials

- Wave function and pseudo wave function of conduction valance band must coincide to each other out of core. Also potential and pseudo potential functions have the same properties.

- Pseudo potential function is not localized outside core, which means it relates to L quantum number.
- We have to consider the charge conservation for both potential and pseudo potentials inside the core.

$$4\pi \int_0^{r_c} \left|\psi_l(\vec{r})\right|^2 r^2 dr = 4\pi \int_0^{r_c} \left|\psi_l^{ps}(\vec{r})\right|^2 r^2 dr$$

- **Wave scattering form core for potential and pseudo potential should be the same. This condition leads to continues of logarithmic derivative of wave function and pseudo wave function at $r = r_c$**

Pseudo wave function in the core region explained as:

$$F_l(\vec{r}) = \vec{r}R(\vec{r}) = r^{l=1} f_l(\vec{r})$$

$$f_l(\vec{r}) = P_l(\vec{r})$$

$$f_l(\vec{r}) = e^{P_l(\vec{r})}$$

$$P_l(\vec{r}) = \alpha_l r^4 + \beta_l r^3 + \gamma_l r^2 + \delta_l$$

$$[\frac{-d^2}{dr^2}+\frac{l(l+1)}{r^2}+V_l^{ps}(\vec{r})-E_l]r^{l+1}\exp(P_l(\vec{r}))=0$$

$$r^{l+1}\exp(P_l(\vec{r}))\Big|_{r=r_c}=\psi_l(\vec{r})\Big|_{r=r_c}$$

$$P_l(\vec{r}_c)=Ln[\frac{\psi_l(\vec{r}_c)}{r_c^{l+1}}]$$

$$[(l+1)r^l+P_l'(\vec{r})r^{l+1}]\exp(P_l(\vec{r})\Big|_{r=r_c}=\psi_l'(\vec{r})\Big|_{r=r_c}$$

$$[(l+1)r^{l-1}+2(l+1)P_l'(\vec{r})r^l+p_l''r^{l+1}+P'^2r^{l+1}]\exp(P_l(\vec{r}))\Big|_{r=r_c}=\psi_l''(\vec{r})\Big|_{r=r_c}$$

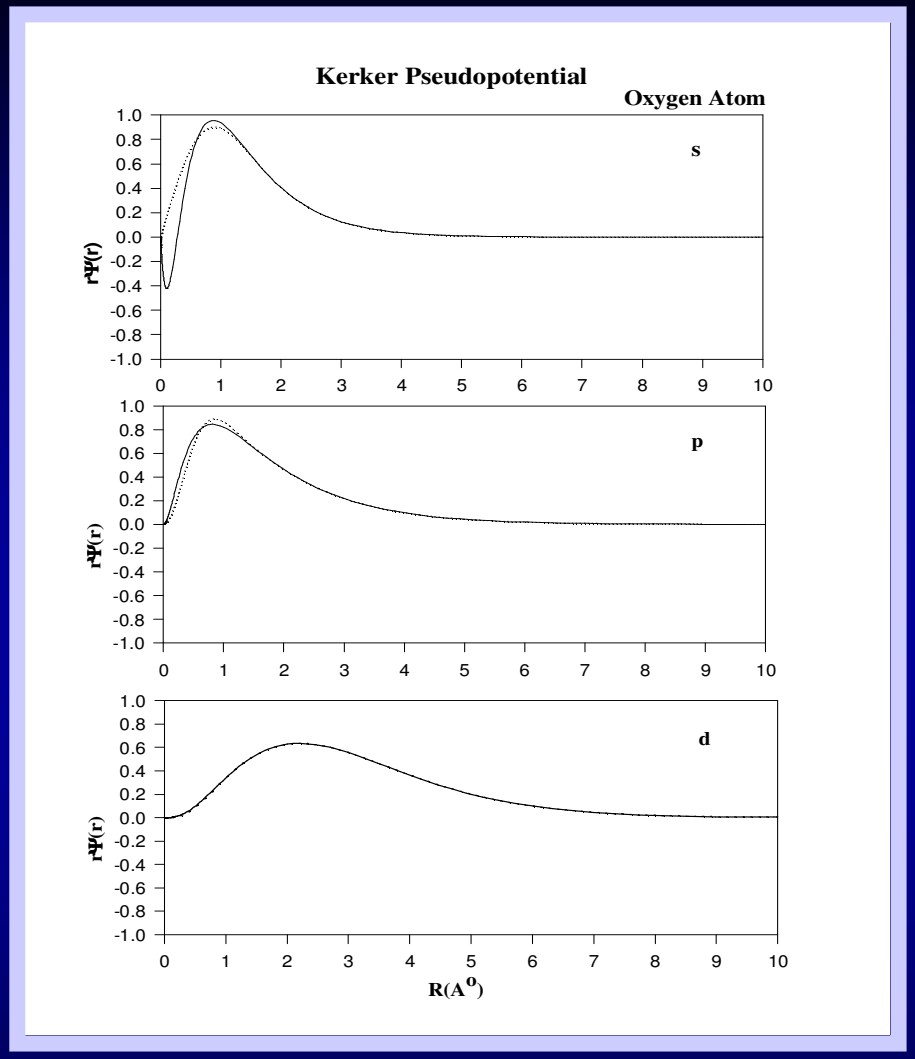
Qc-tuning method

This method is an extended of optimum procedure for producing pseudo potential.

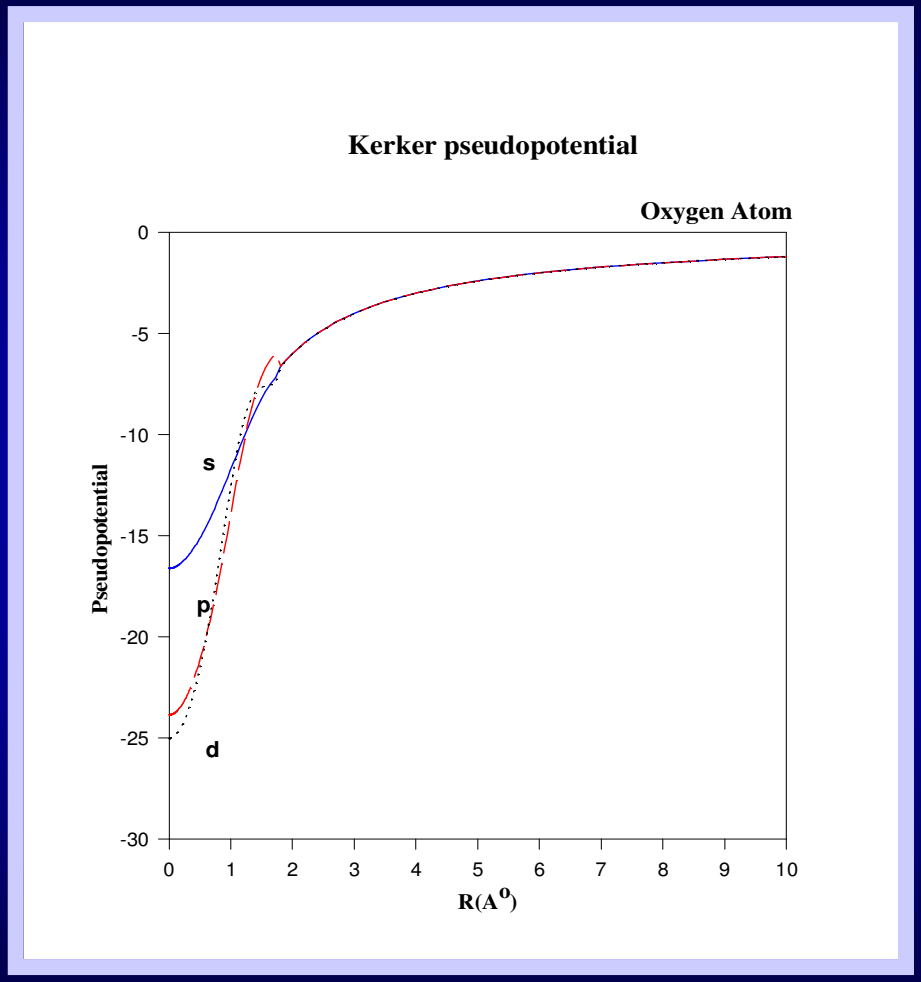
Rap and his co-worker,1990,presented a method called RRKJ. They choose the pseudo wave function of valence electrons as a linear combination of Bessel equation.
First we produce the pseudo wave function and then by using reciprocal schrodinger equation, we calculate the pseudo potential.

$$\psi_l^{ps}(\vec{r}) = \sum_{i=1}^{n} \alpha_i j_l(q_i \vec{r}) \qquad r < r_c$$

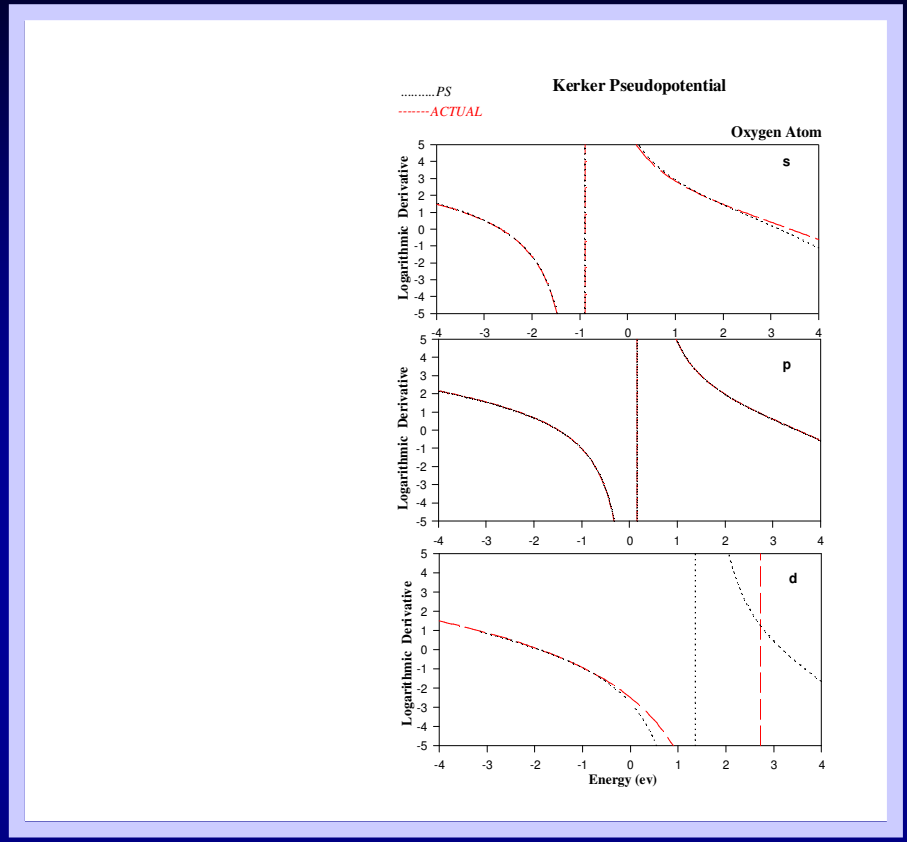
$$\psi_l^{ps}(\vec{r}) = \psi_l(\vec{r}) \qquad r \geq r_c$$



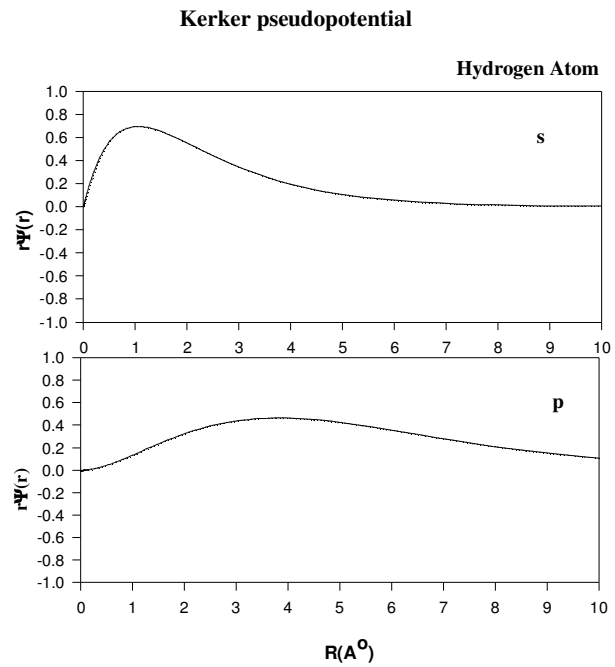
Wave function and pseudo wave function of S,P and D orbital of oxygen atom produced by Kerker method.

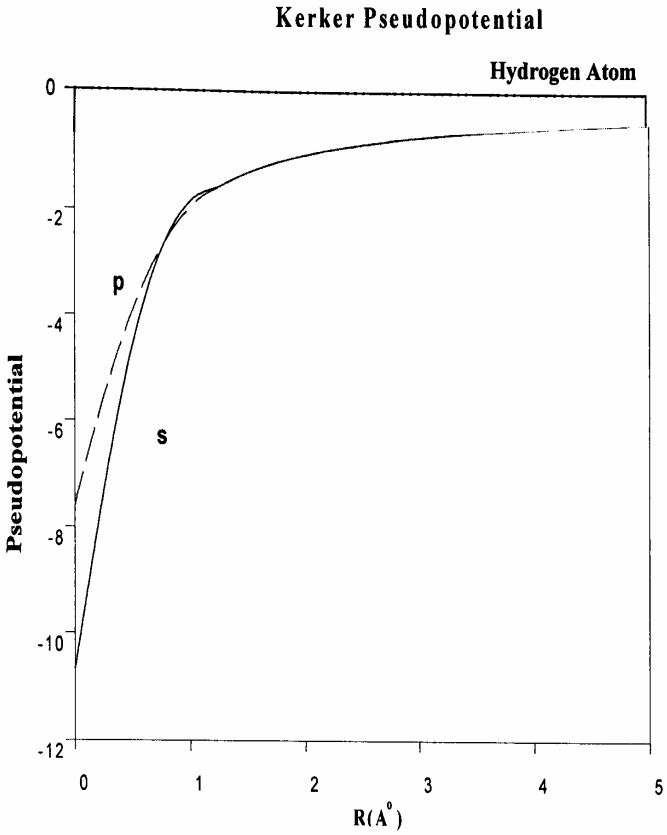


Potential and pseudo potential of S,P and D orbitals of oxygen atom produced by Kerker method.



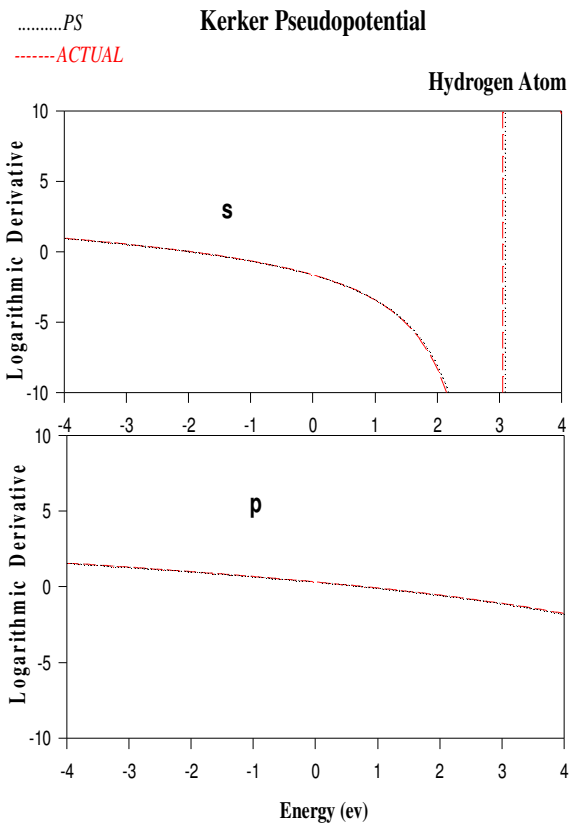
Logarithmic derivative of real potential and pseudo potential of S,P and D orbitals of oxygen perused



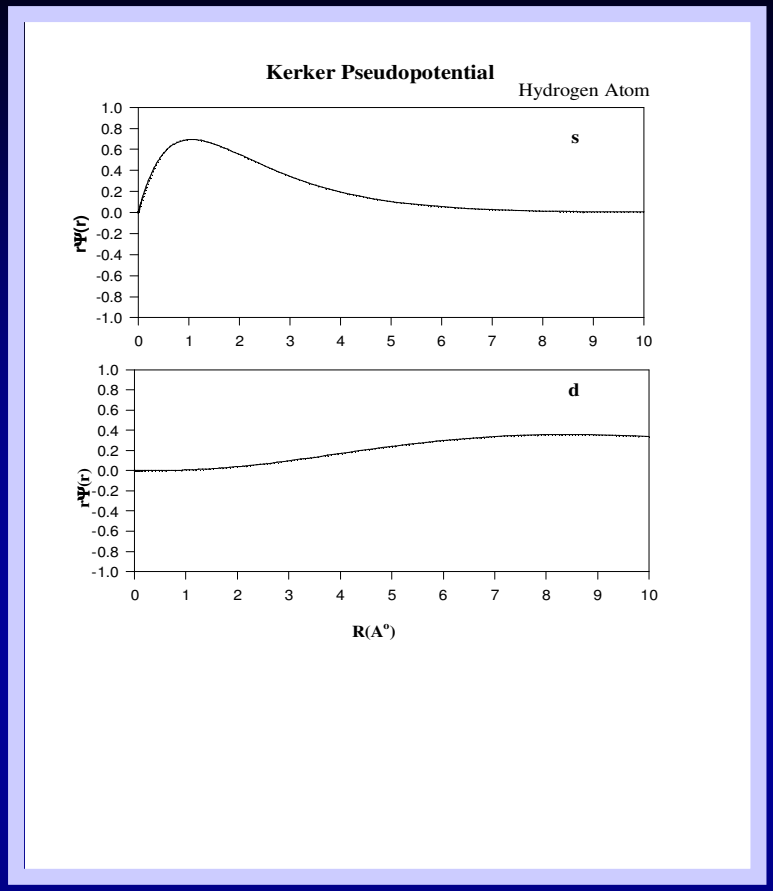


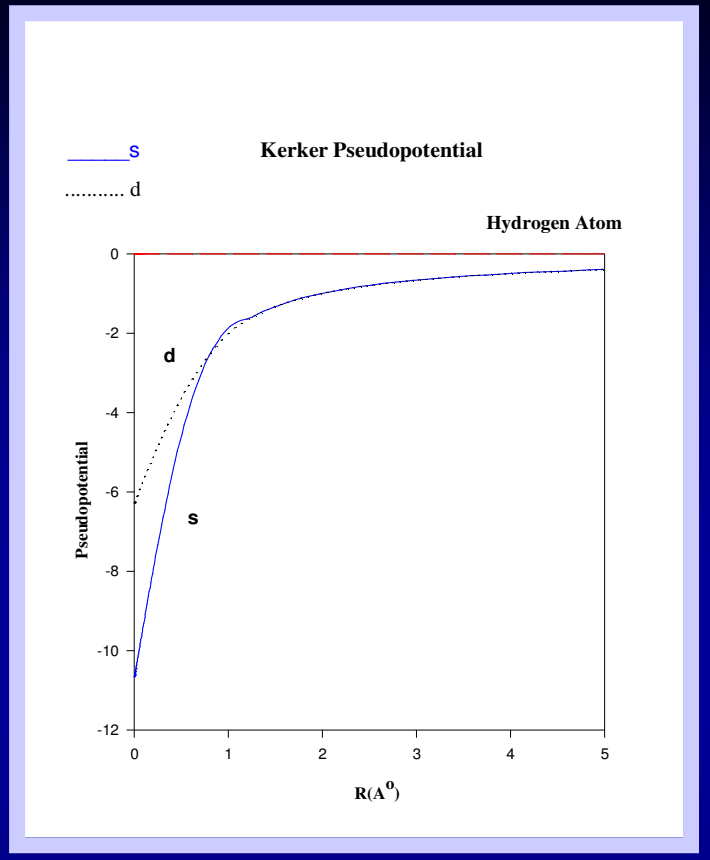
(Left)-Wave function and pseudo wave function of S,P orbitals of hydrogen atom.

(right)- Potential and pseudo potential of S and P orbitals of hydrogen atom.



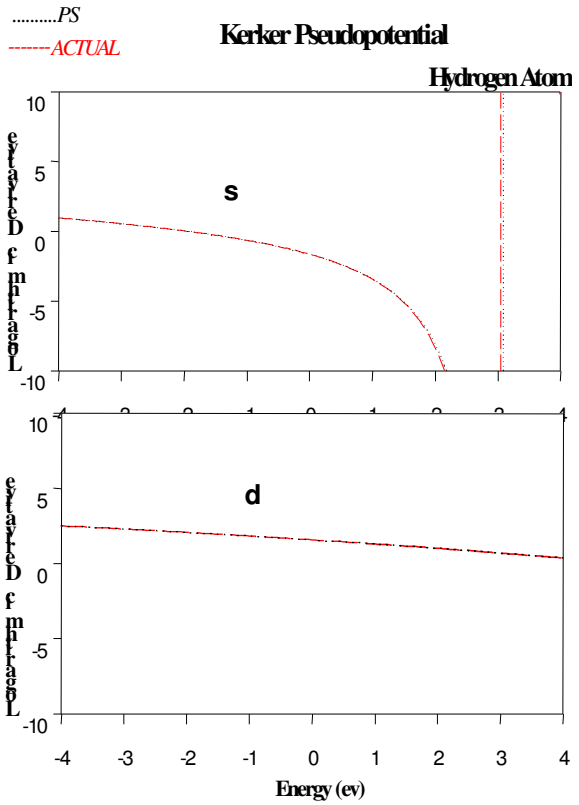
Logarithmic derivative of real potential and pseudo potential of S and P orbitals of hydrogen



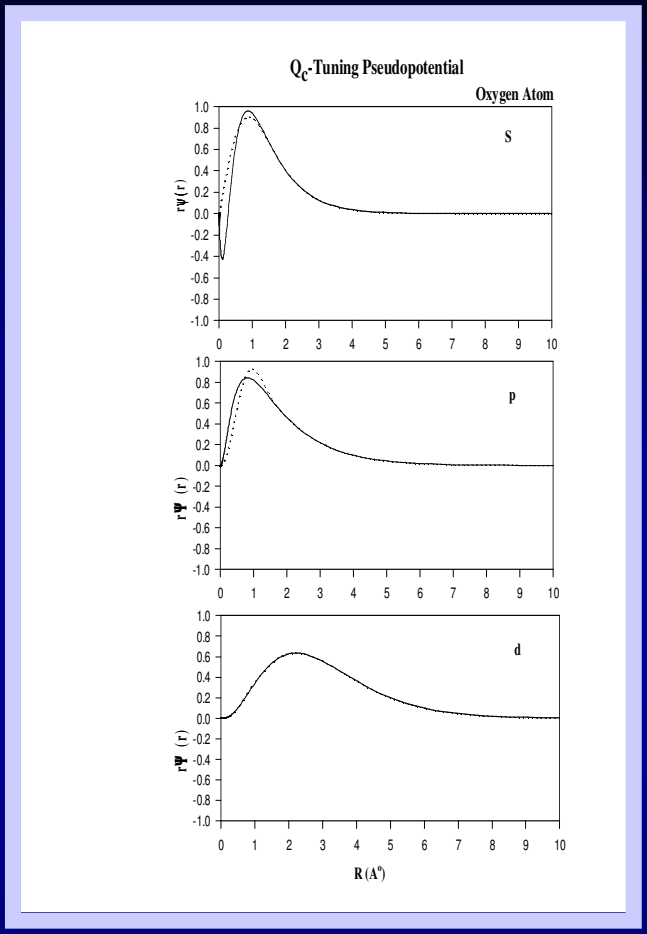


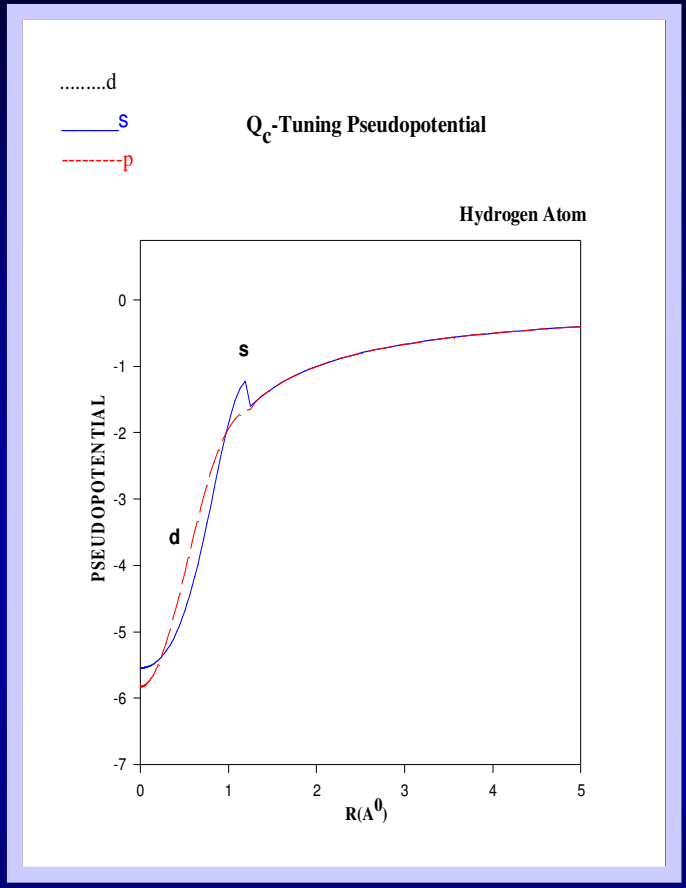
(Left)-Wave function and pseudo wave function of S,D orbitals of hydrogen atom.

(right)- Potential and pseudo potential of S and D orbitals of hydrogen atom.



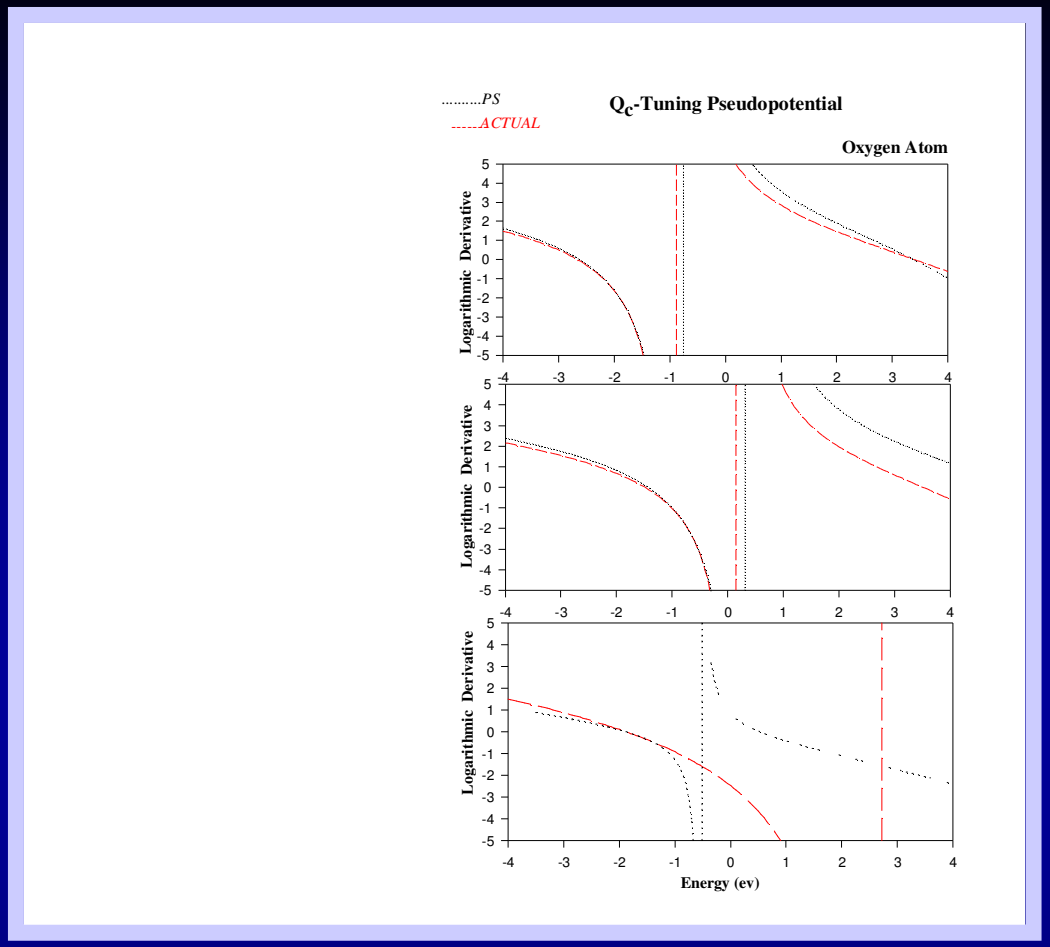
Logarithmic derivative of real potential and pseudo potential of S and P orbitals of hydrogen.



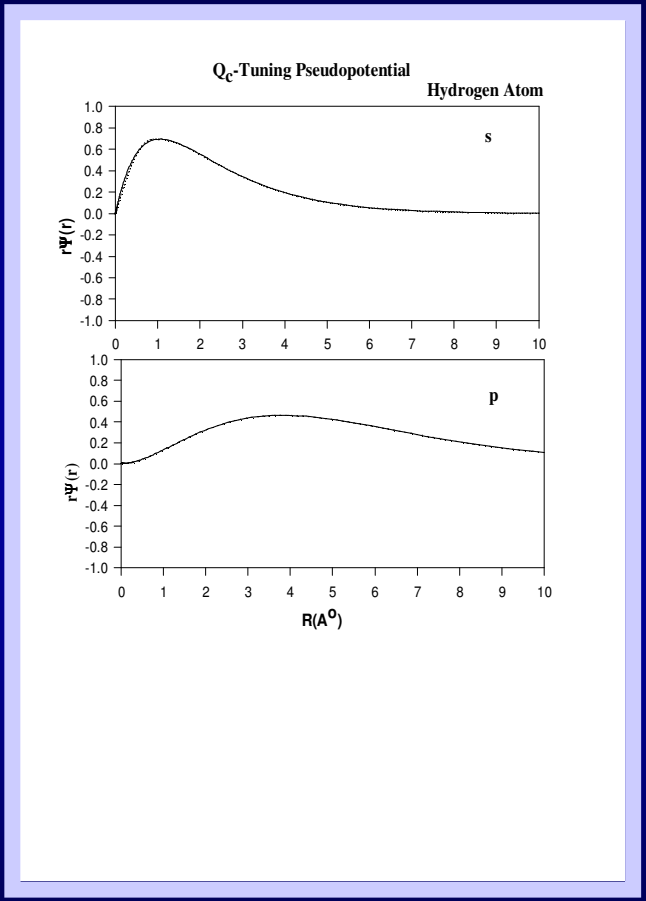


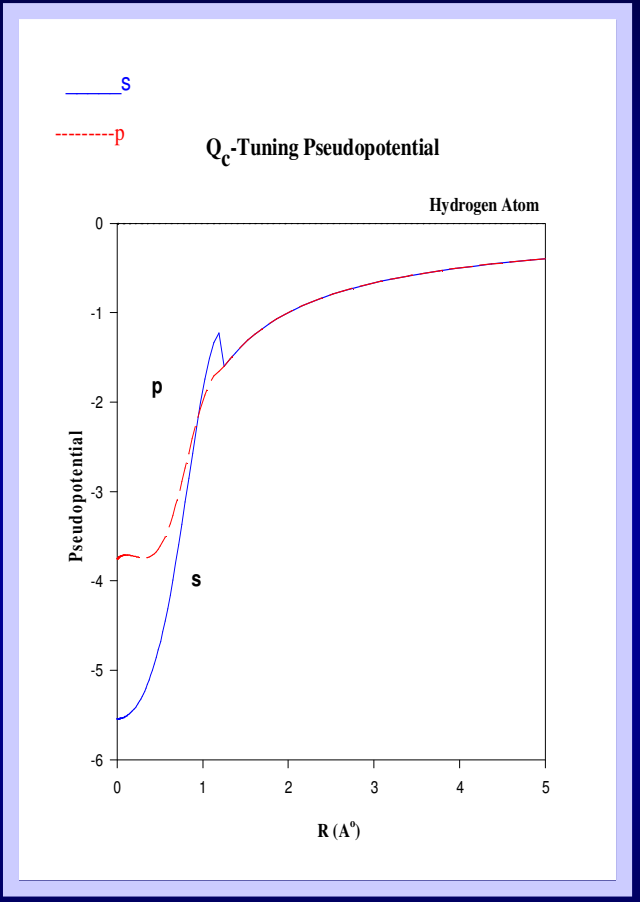
(Left)-Wave function and pseudo wave function of S,P orbitals of oxygen atom.

(right)- Potential and pseudo potential of S and d orbitals of hydrogen atom.



Logarithmic derivative of real potential and pseudo potential of S and P orbitals of oxygen perused by Qc-tuning method





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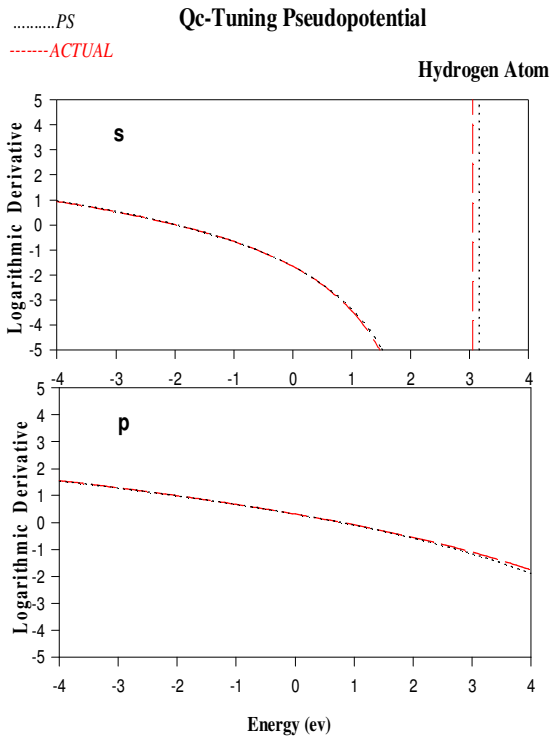
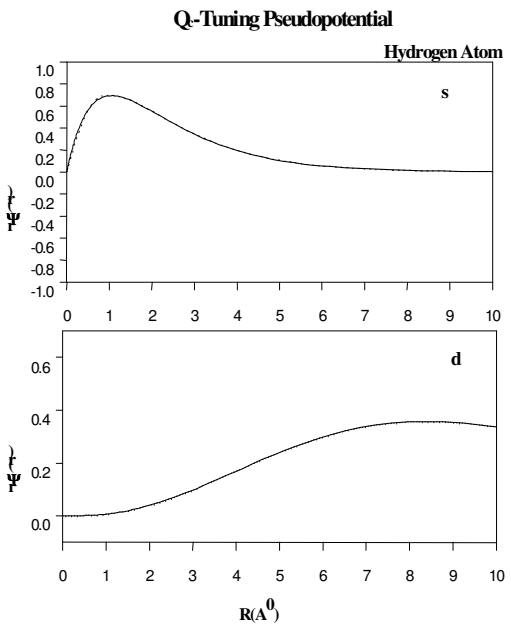
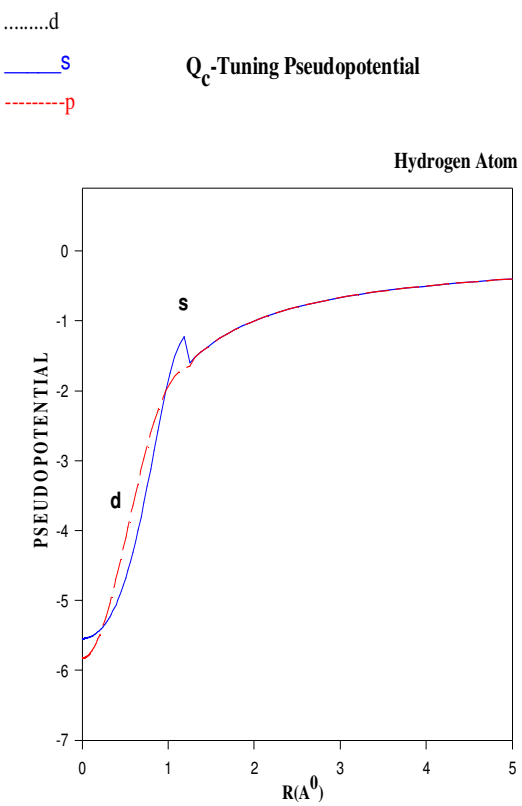


Logarithmic derivative of real potential and pseudo potential of S and P orbitals of hydrogen.





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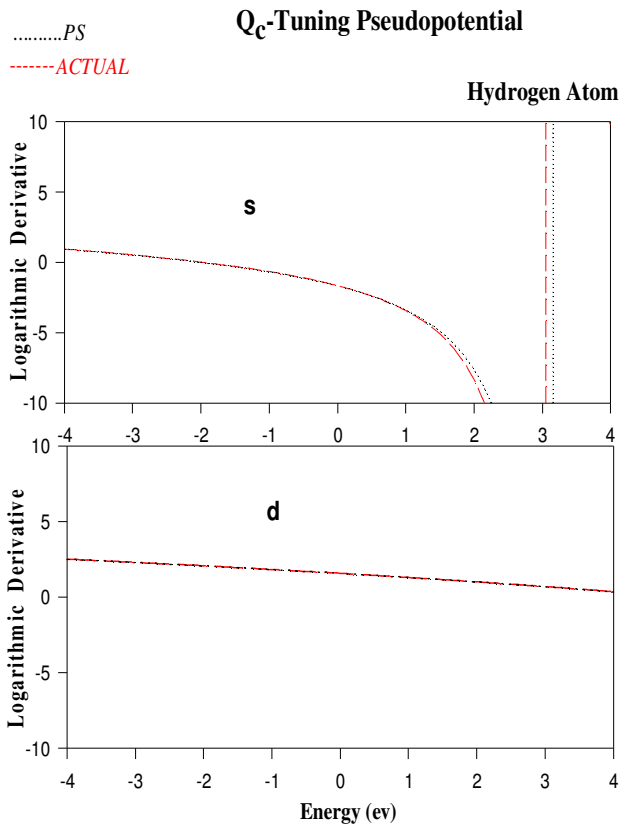
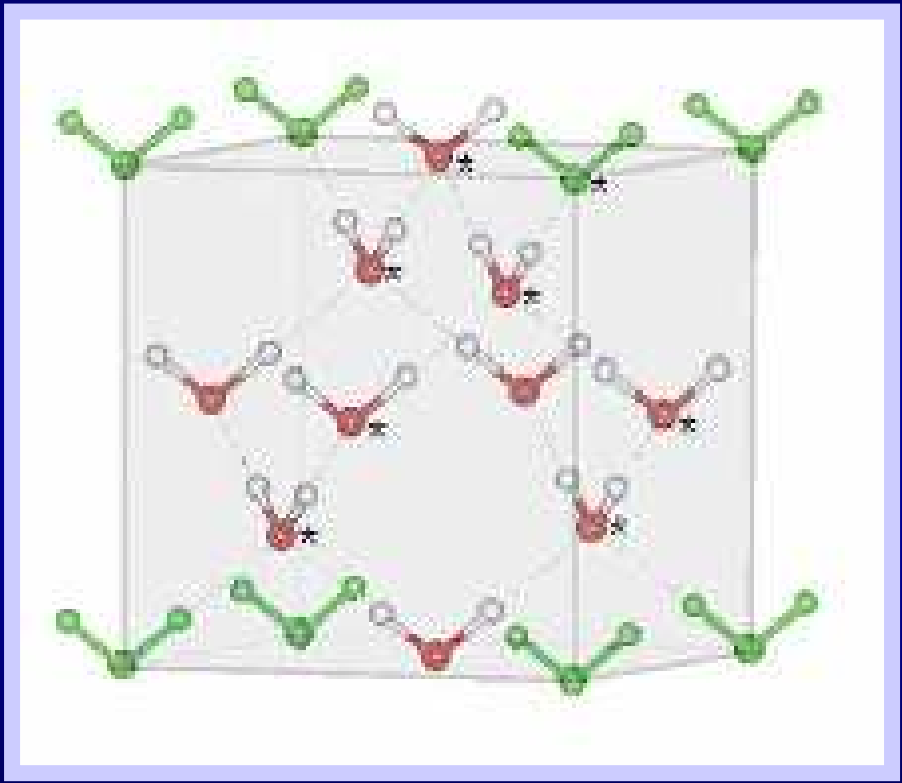
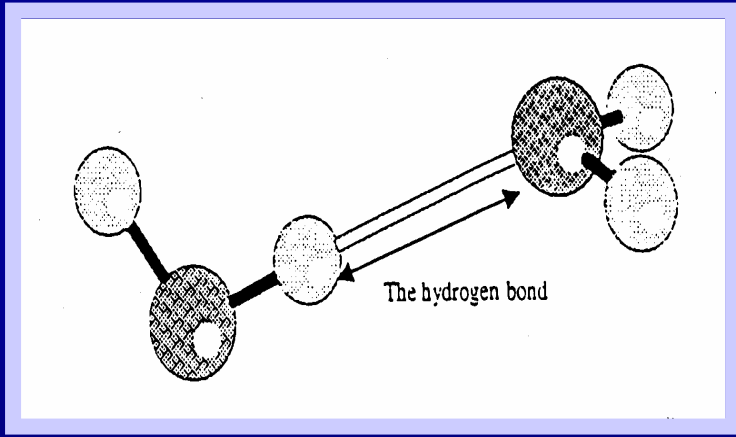


Logarithmic derivative of real potential and pseudo potential of S and D orbitals of hydrogen.

For minimizing the energy of each configuration and structural parameter identification, we do need to determine the positions of atoms and use them as an input for calculation





Positions of atoms in four different configurations of cubic ice

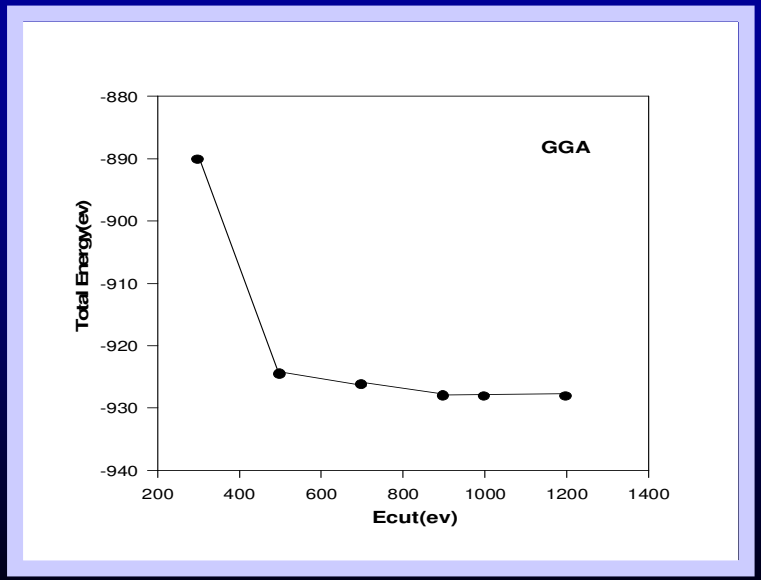
1			2			3			4		
0.29160	0.29160	0.30827	0.29160	0.29160	0.30827	0.29160	0.29160	0.30827	0.29160	0.29160	0.30827
0.95832	0.95832	0.30827	0.95832	0.95832	0.30827	0.04168	0.04168	0.22506	0.95832	0.95832	0.30827
0.04168	0.20840	0.05835	0.04168	0.20840	0.05835	0.95831	0.29160	0.97498	0.04168	0.20840	0.05835
0.20840	0.04168	0.05835	0.20840	0.04168	0.05835	0.20840	0.04168	0.05835	0.20840	0.04168	0.05835
0.45832	0.45832	0.30827	0.45832	0.45832	0.30827	0.45831	0.45832	0.30827	0.54168	0.54168	0.22506
0.79160	0.79160	0.30827	0.70839	0.70839	0.22506	0.79160	0.79160	0.30827	0.70839	0.70839	0.22506
0.70840	0.54168	0.05835	0.79160	0.45831	0.97499	0.7084	0.5417	0.05835	0.79160	0.45831	0.97498
0.54168	0.70840	0.05835	0.54168	0.70840	0.05835	0.5417	0.7084	0.05835	0.4583	0.79160	0.97498
0.54168	0.20840	0.55835	0.54168	0.20840	0.55835	0.5417	0.2084	0.55835	0.4583	0.29160	0.47498
0.70840	0.04168	0.55835	0.79160	0.95831	0.47498	0.79160	0.95831	0.47498	0.79160	0.95831	0.47498
0.79160	0.29160	0.80827	0.70839	0.20839	0.72506	0.70839	0.20839	0.72506	0.70839	0.20839	0.72506
0.45832	0.95832	0.80827	0.45832	0.95832	0.80827	0.45832	0.9583	0.8083	0.5417	0.04168	0.72506
0.20840	0.54168	0.55835	0.20840	0.54168	0.55835	0.20840	0.54168	0.55835	0.20840	0.54168	0.55835
0.04168	0.70840	0.55835	0.04168	0.70840	0.55835	0.04168	0.70840	0.55835	0.04168	0.70840	0.55835
0.95832	0.45832	0.80827	0.95832	0.45832	0.80827	0.95832	0.45832	0.80827	0.95832	0.45832	0.80827
0.29160	0.79160	0.80827	0.29160	0.79160	0.80827	0.29160	0.79160	0.80827	0.29160	0.79160	0.80827
0.12504	0.12504	0.14171	0.12504	0.12504	0.14171	0.12504	0.12504	0.14171	0.12504	0.12504	0.14171
0.62504	0.62504	0.14171	0.62504	0.62504	0.14171	0.62504	0.62504	0.14171	0.62504	0.62504	0.14171
0.62504	0.12504	0.64171	0.62504	0.12504	0.64171	0.62504	0.12504	0.64171	0.62504	0.12504	0.64171
0.12504	0.62504	0.64171	0.12504	0.62504	0.64171	0.12504	0.62504	0.64171	0.12504	0.62504	0.64171
0.37496	0.37496	0.39163	0.37496	0.37496	0.39163	0.37496	0.37496	0.39163	0.37496	0.37496	0.39163
0.87496	0.87496	0.39163	0.87496	0.87496	0.39163	0.87496	0.87496	0.39163	0.87496	0.87496	0.39163
0.87496	0.37496	0.89163	0.87496	0.37496	0.89163	0.87496	0.37496	0.89163	0.87496	0.37496	0.89163
0.37496	0.87496	0.89163	0.37496	0.87496	0.89163	0.37496	0.87496	0.89163	0.37496	0.87496	0.89163

Total energy versus cut off energy with Qc-tuning method and GGA approximation

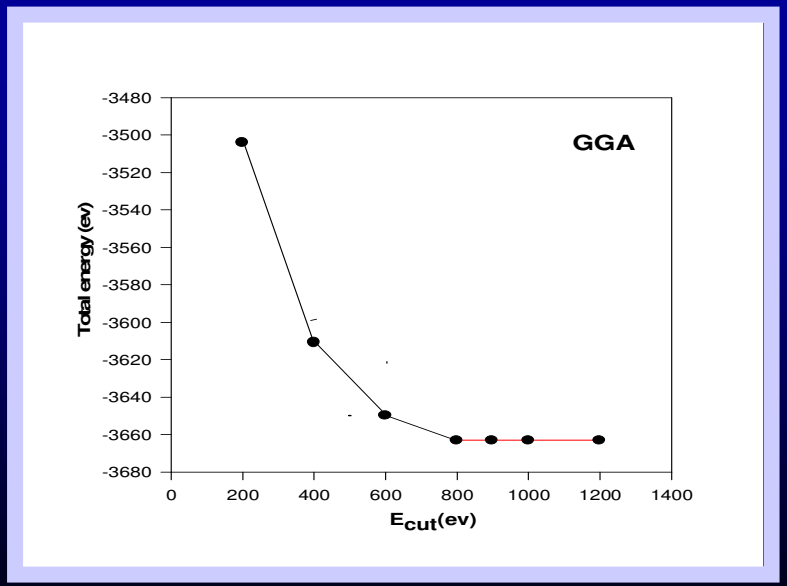
Ecut(ev)	Ecut=900ev	Ecut=1200ev
Unit cell(ev)	-922.0355	-922.0743
Convectional cell	-3728.1420	-3728.1091

- Total energy versus cut of energy obtained by Qc-tuning and GGA approximation

(unit cell)



(conventional cell)

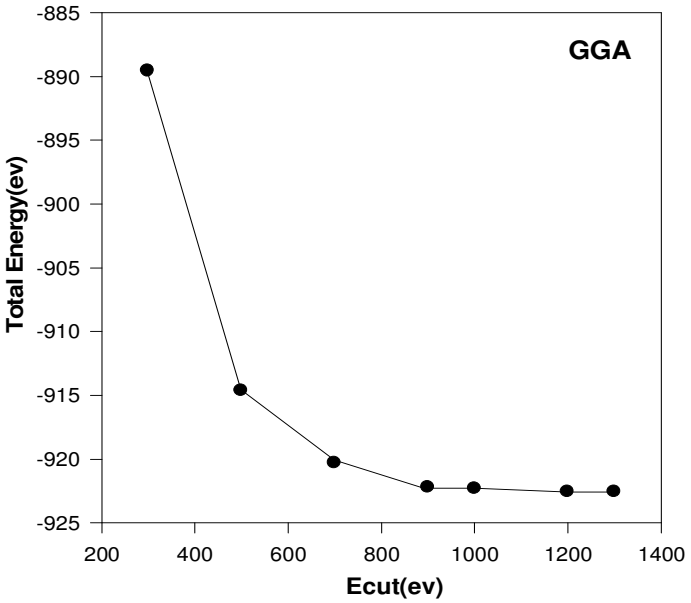


Total energy versus cut off energy with Kerker method and GGA approximation

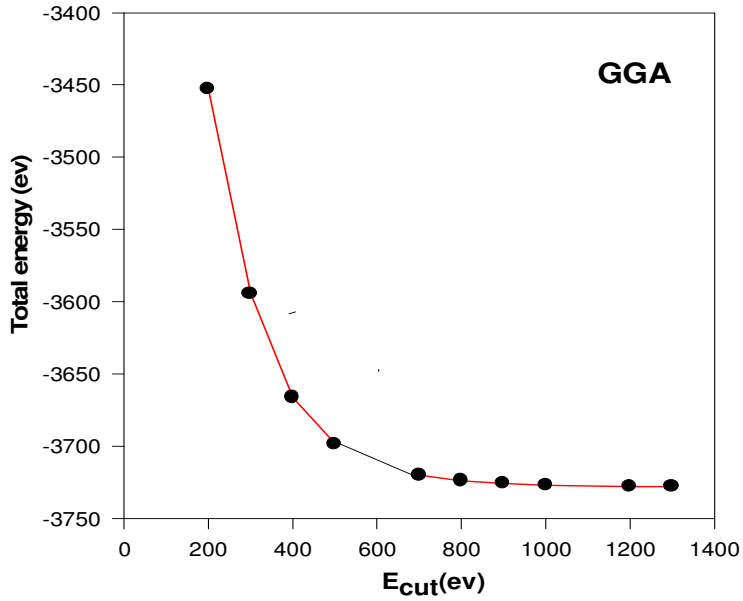
cut of energy (ev)	Ecut=1200	Ecut=1300
unit cell energy(ev)	-928.165250	-928.1509
Convectional cell(ev)	-3726.7590	-3726.7754

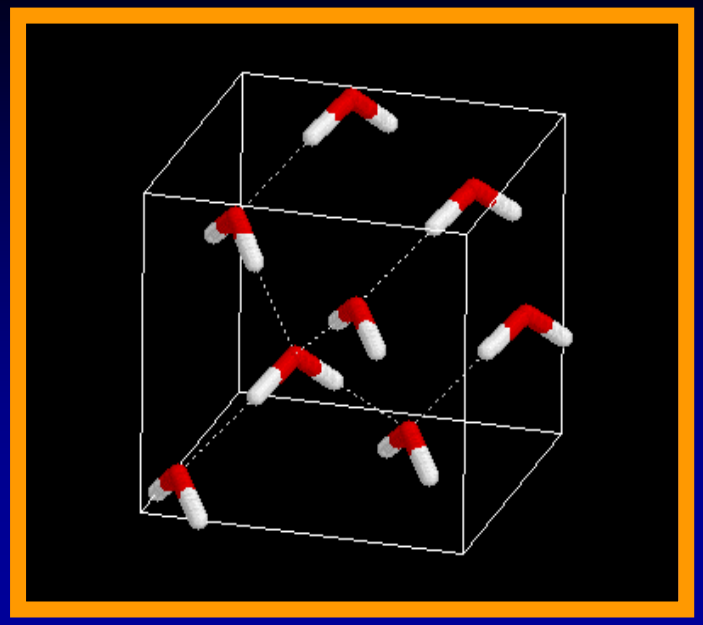
Total energy versus cut off energy obtained by Kerker method

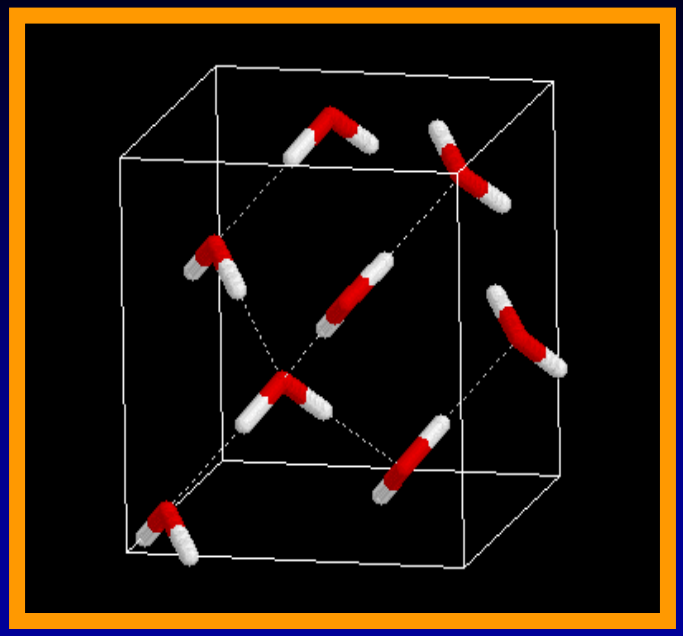
unit cell

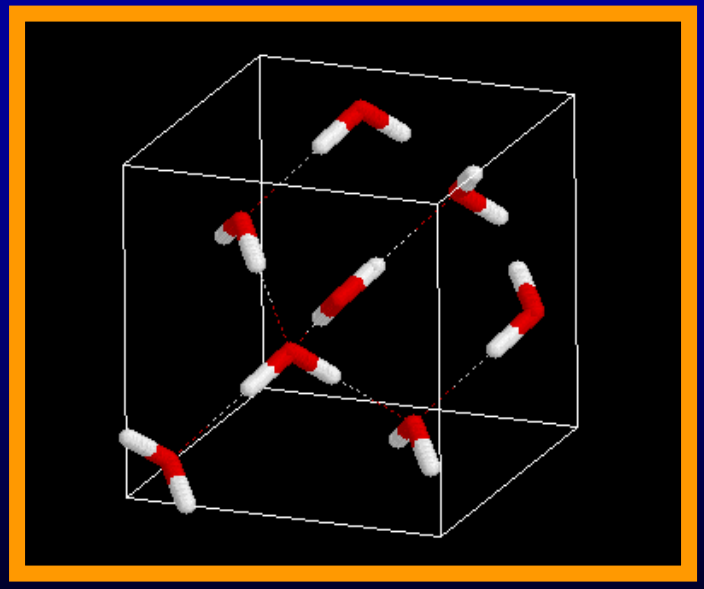


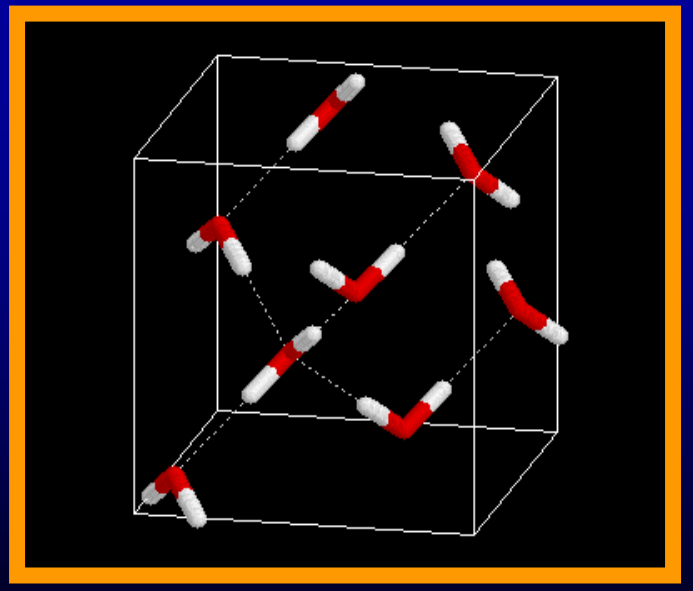
conventional cell









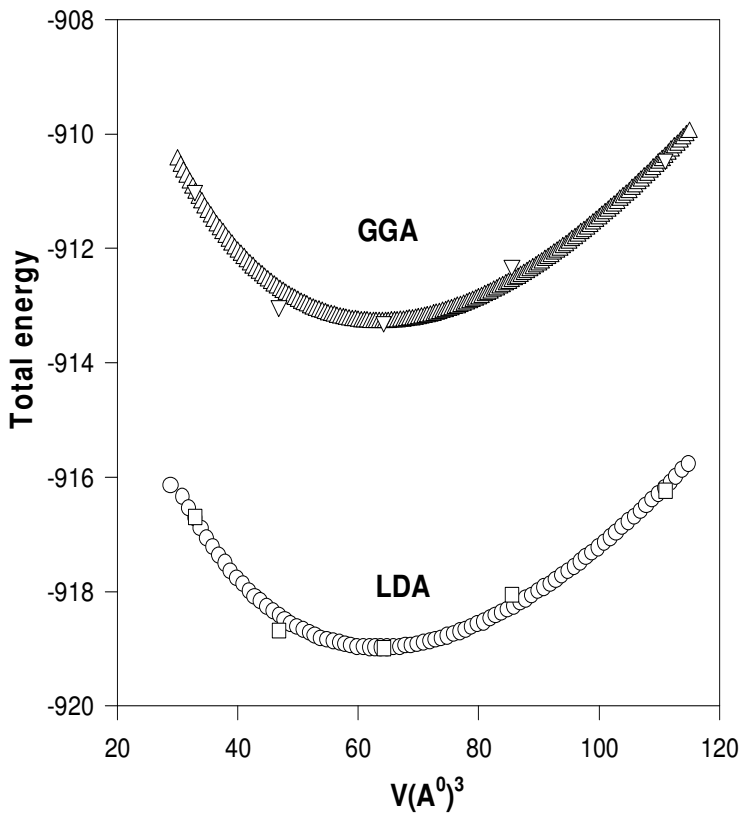


Comparison of total energy of four different configurations of cubic ice phases

Configuration	1	2	3	4
Calculated energy(ev)	-3686.7968	-3685.9682	-3685.9413	-3685.9369
Energy (ev) (by other)	-3745.761838	-3745.74815	-3745.74040	-3745.733617

Total energy (ev) for unit cell and conventional cell:

Cut of energy	Unit cell energy	Unit cell energy*4	Convectional cell energy
Total energy by Qc-method [Ecut=900]	-919.050	-3676.2	-3686.81
Total energy by Kerker [Ecut=1200]	-935.258	-3741.032	-3750.03



The total energy versus volume for unit cell calculation and Qc-tuning method

Parameters obtained by Qc-tuning for unit cell without motion of Ion

approach	Bo	Bop	Eo	Vo	a(Å)	error
LDA	0.08614	4.2567	-908.627	84.6671	6.9704	9.62
GGA	0.1291	4.8201	-914.577	74.6789	6.684762	5.128

Parameters obtained by Qc-tuning for unit cell with motion of Ion

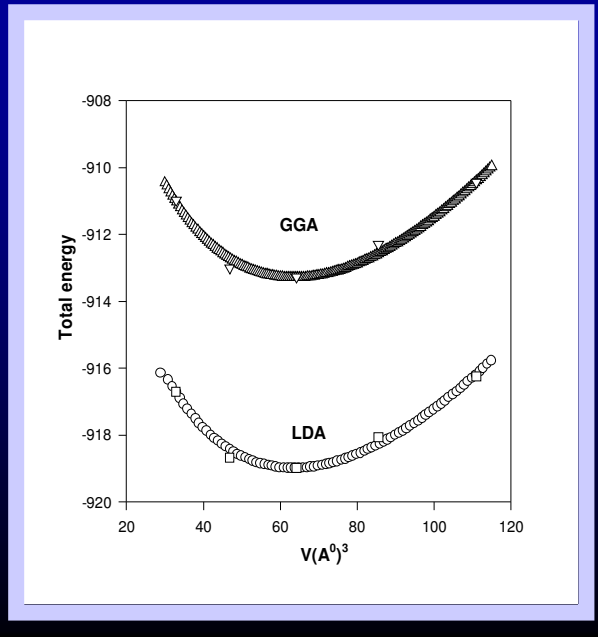
approach	Bo	Bop	Eo	Vo	a(A)	error
LDA	0.2208	1.0102	-912.206	62.6117	6.2267	0.22
GGA	0.2152	1.0398	-919.050	62.6117	6.3367	0.22

The effect of D and P orbitals of hydrogen atom on structure parameter

Structural parameters obtained by using unite cell and d orbital of hydrogen atom in pseudo potential in Qc-tuning method…

approach	Bo	Bop	Eo	Vo	a(A)	error
GGA	0.2261	0.993548	-918.989	62.6117	6.3367	0.33
LDA	0.21256	1.5232	-912.290	63.6117	6.3367	0.33

Total energy versus volume for unite cell using d orbital of H atom and Qc-tuning method

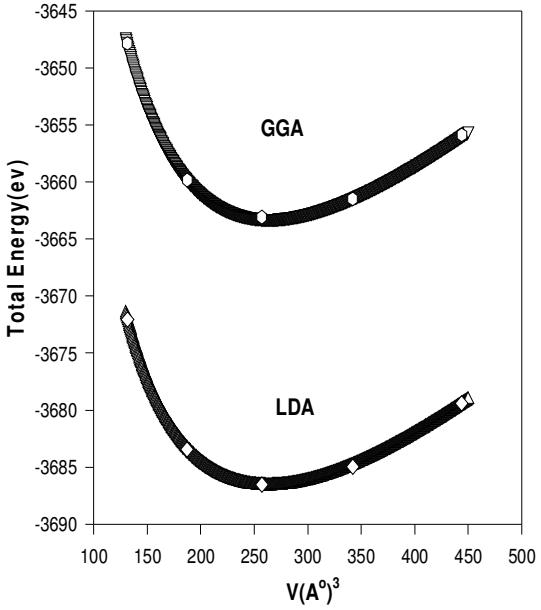


Effect of various of Rc in structural properties of cubic ice

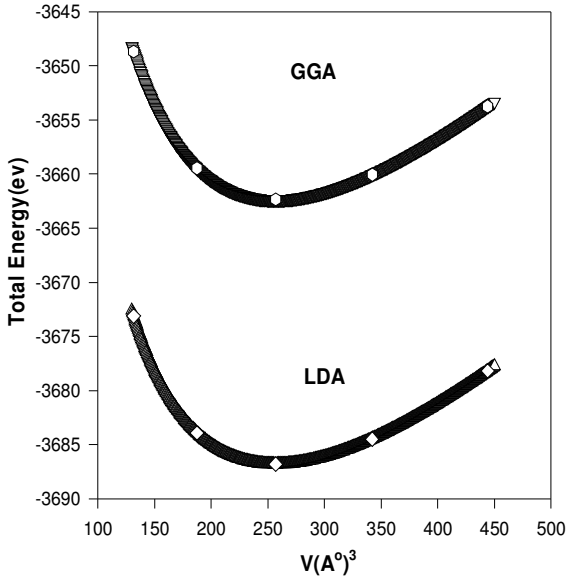
Variation of structural parameters versus cut off radius for GGA approximation and Qc-tuning method in calculation of unit cell

	Bo	Bop	Eo	Vo	a (Å)	error
Rc(s,p,d)H=1.228(a.u) Rc(s,p,d)O=1.5(a.u)	0.10228	2.68876	-927.219	109.921	7.6040	19.59
RcH=1.15(a.u) RcO=1.8(a.u)	0.271728	1.39205	-918.132	63.6117	6.337	0.33
Rc(s,p)H=1.228(a.u) Rc(d)H=1.25(a.u) Rc(s,p,d)O=1.8(a.u)	0.3189	0.6517	-919.001	63.6117	6.3367	0.33

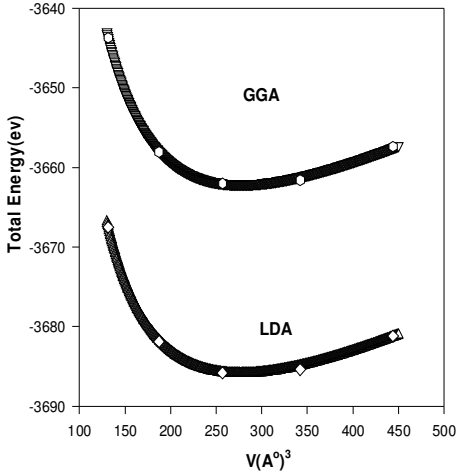
0.97 Angstrom



0.92 Angstrom



Length of O-H band
0.95 Angstrom



- The curves of total energy versus volume of conventional cell computed from pseudo potential obtained by Qc-tuning method

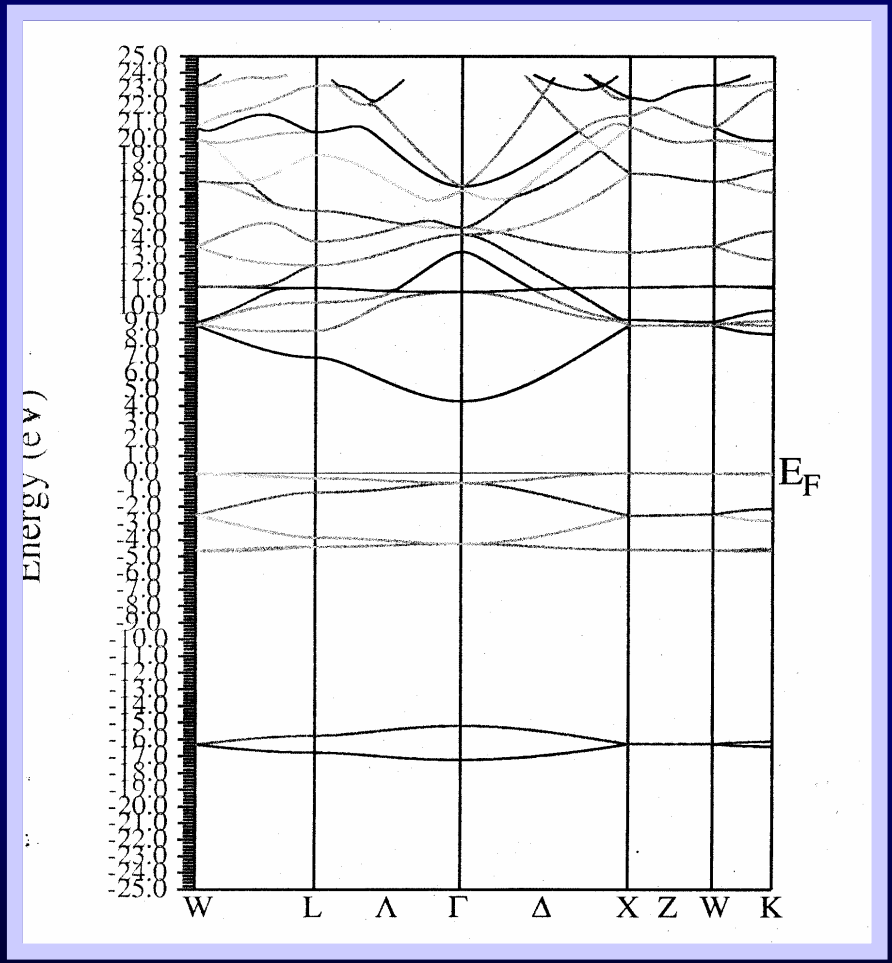
Calculated length of O-H band for cubic ice

Different values for it has been reported

O-H(Å)	Bo	Bop	Eo	Vo	a(Å)
0.97	0.222481	2.12172	-3686.81	256.798	6.3562
0.95	0.203654	2.28705	-3686.62	263.466	6.4107
0.93	0.1665	2.9881	-3685.93	277.047	6.5190

The length of O-H band is 0.97 Å

The Band Structure of cubic ice obtained by Wien2k soft wear. The gap energy is 5.4 ev



Conclusion:

A)- We find the right configuration for Cubic Ice.

B)-To compute exchange correlation energy, GGA and LDA approximations reach to the same value, but cell parameter which obtained by GGA method is slightly closer to the experimental value.

C)-In pseudo potential calculation there will be no different in the outcome results if we consider p or d for exited state of hydrogen atom.

D)- Structural determination for unit cell and conventional cell gives the same results which indicated that the positions of atoms have been calculated correctly.

E)- We deduce the length of O-H band in cubic Ice which is 0.97 angstrom.


The end

Minimizing the functional energy:

1- Solution to single equations of Kohn-Shem for single particle
2- Conjugate gradient procedure

$$F(x)=F(x)+(x-x_o)\nabla F(x_o)+\frac{1}{2}(x-x_o)^T\frac{\partial^2 F}{\partial x_i \partial x_j}\Big|(x-x_o)$$

لخت کردن شبه پتانسيل

شبه پتانسيل بدست آمده براي اتم منزوي است و براي استفاده آن در بلور بايد حالت اتمي را حذف و معادل بلوري را اضافه کنيم . به اين منظور چون تفاوت بين پتانسيل اتم منزوي و اتم واقع درز بلور ، ناشي از تفاوت در توزيع ابر الکتروني آنهاست پتانسيل هاي تبادلي همبستگي و هارتري به علت وابستگي به چگالي ابر الکتروني

متفاوت خواهند بودو بايد اين دو جمله را از پتانسيل کم کرد.

$$V_l^{ps^{Unscreen}}(\vec{r}) = V_l^{ps}(\vec{r}) - \{V_H[n(\vec{r})] + V_{xc}[n(\vec{r})]\}$$

چون پتانسيل هارتري ناشي از برهمکنش کولني الکترونهاست، مي توان آنرا به صورت جداشده زير نوشت:

$$V_H(n_{core}(\vec{r}) + n_{val}(\vec{r})) = V_H(n_{core}(\vec{r})) + V_H(n_{val}(\vec{r}))$$

ولي اين خاصيت در مورد سهم Vxc در شبه پتانسيل صادق نيست و نمي توان آنرا بصورت جداشده نوشت.با اعمال تقريب حذف بر همکنش تبادلي همبستگي بين الکترونهاي مغزه و ظرفيت ، هيچ گونه ارتباطي بين الکترونهاي مغزه و ظرفيت وجود نخواهد داشت .در نتيجه جمله نيزبه صورت جداشده اي در خواهد آمد .چون تغيير چگالي بار الکترون اتم منزوي نسبت به اتم واقع در بلور عملا ناشي از الکترونهاي ظرفيت است،داريم:

$$V_l^{ps^{Unscreen}}(\vec{r}) = V_l^{ps}(\vec{r}) - \{V_H[n_{val}(\vec{r})] + V_{xc}[n_{val}(\vec{r})]\}$$

شبه پتانسيل بايد هموار و صحيح باشد .در اين روش قيد پيوستگي مشتق دوم برداشته شده و متغير ديگري وارد مسئله مي شود كه با تغيير آن ميزان انطباق مشتق لگاريتمي و پيوستگي پتانسيل و شبه پتانسيل در rc تعيين مي شود.

One of the problems in Hearty approximation is that with changing the positions of electrons in the system,the total wave function is not ant symmetry,and the Pouli rule is not valid.

To solve this problem fock:

$$\psi(\vec{r}_1,\vec{r}_2,...,\vec{r}_3)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_1(\vec{r}_1) & \psi_1(\vec{r}_1) & ...\psi_1(\vec{r}_N)\\ \psi_2(\vec{r}_1) & \psi_2(\vec{r}_2) & ...\psi_2(\vec{r}_N)\\ ... & & \\ \psi_N(\vec{r}_1) & \psi_N(\vec{r}_2) & ...\psi_N(\vec{r}\ )\end{vmatrix}$$

$$\psi_i(\vec{r}_i)=\varphi_i(\vec{r}_i)\chi_i(\sigma)$$

شبه پتانسيل هاي ابتدا به ساكن(Ab initio)

محاسبات آن بر پايه اوليه كوانتمي استوار است. در اين روش محاسبات براي يك اتم منزوي انجام مي گيرد و سپس براي بررسي ساختار بلوري از شبه پتانسيل هاي عناصر تشكيل دهنده بلور استفاده مي شود. در توليد شبه پتانسيل ابتدا به ساكن از هيچگونه تقريب و نتايج تجربي استفاده نمي شود و براي توليد اين شبه پتانسيل از دو روش استفاده مي شود.

1-شبه پتانسيل هايي كه در محاسبه آن ها ابتدا با بكار بردن پتانسيل در معادله شرودينگر اتم منزوي و حل خودسازگار آن نخست پتانسيل واقعي را به دست مي آورند و سپس شبه پتانسيل از روي آن ساخته مي شود. حل معادله شرودينگر براي اين شبه پتانسيل منجر به توليد شبه تابع موج مي شود. مثل روش BHS كه در سال 1982 توسط بچلت، هامن واشلوتر براي 52 عنصر با اين روش شبه پتانسيل توليد شد. اين نظريه ابتدا توسط هامن، اشلوتر و چيانگ در سال 1979 ارائه شد.

2-شبه پتانسيل هايي كه با بكار بردن پتانسيل و تابع موج واقعي اتم منزوي ابتد اشبه تابع موج و سپس به كمك معادله شرودينگر وارون شبه پتانسيل توليد مي شود، مثل روش كركر كه در سال 1982 توسط كركر ارائه شد

For structural determination we have to put pressure on the crystal. We increase and decrease the cell parameter and using Mornagon equation of state.

$$E[v] = \frac{BV}{B}\left[\frac{\left(\frac{V_o}{V}\right)^{B'_o}}{B'_o - 1} + 1\right] + cte$$