YÜKSEK BAŞARIMLI HESAPLAMALARLA GÜNCEL KİMYASAL PROBLEMLERİN ÇÖZÜMÜ

TEPKİMELERDE ELEKTRONLARIN DAVRANIŞI NASIL MODELLENİR?

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Kimya ≈ “Elektronlar ne yapıyor?”

Schrödinger denklemini çöz! – Zor!

Yaklaşık çöz, analitik değil nümerik olsun.

Orbital yaklaşımı

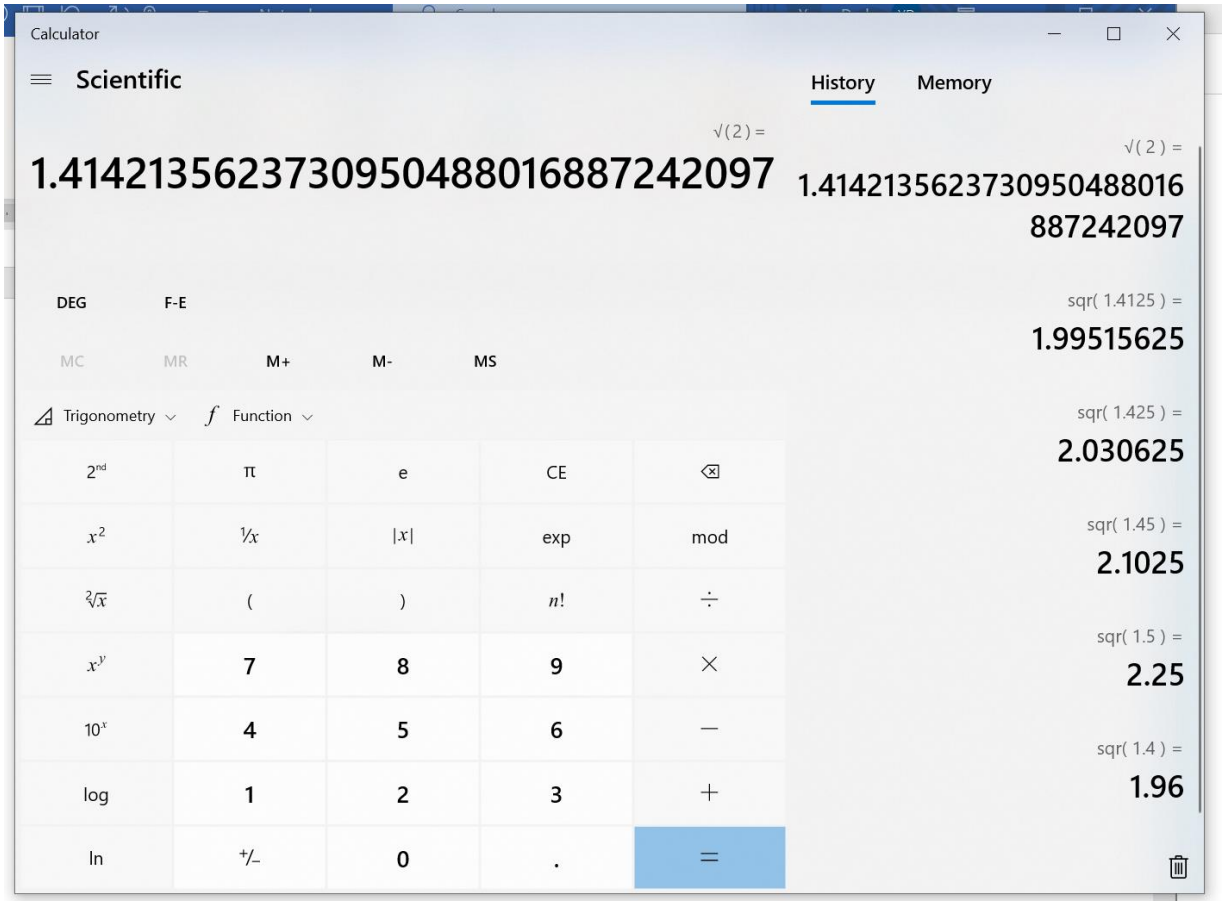
Süper bilgisayarlar

$$\hat{H}\Psi = E\Psi$$

Schrödinger
1926

Yaklaşık çözüm

Analitik değil nümerik olsun.
Ör. $x^2 - 2 = 0$



Yüksek başarımlı hesaplama sistemleri (Süper bilgisayarlar)

Hesaplamalı kimya:

Dalga fonksiyonu postülatı, Ψ
Operator – özdeğer postülatı

Schrödinger denklemi:

$$\widehat{H\Psi} = i\hbar \frac{\partial \Psi}{\partial t}$$

$$\widehat{H\Psi} = E\Psi$$

Orbital yaklaşımı

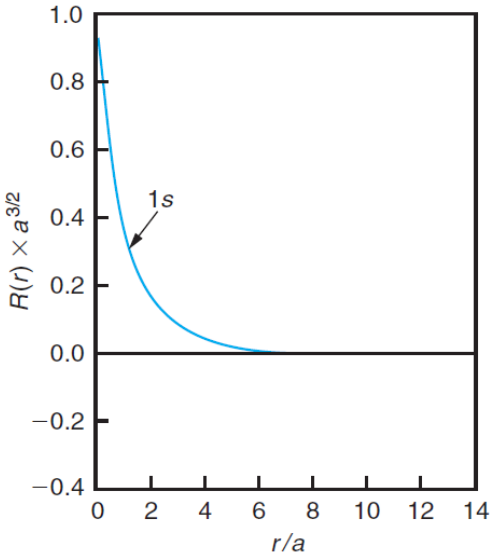
TR-Grid

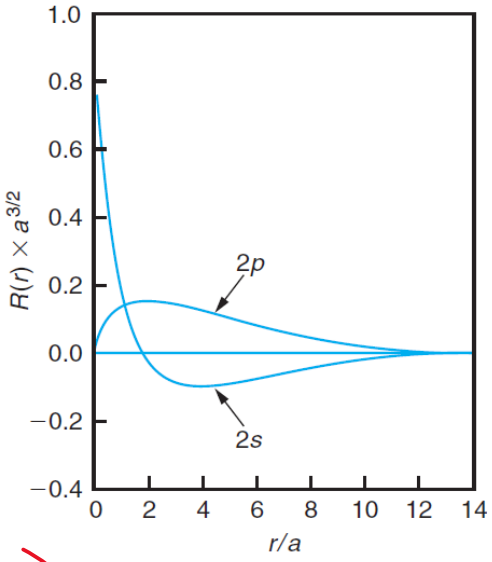
H(benzeri)-atom Dalga Fonksiyonları/Orbitaller

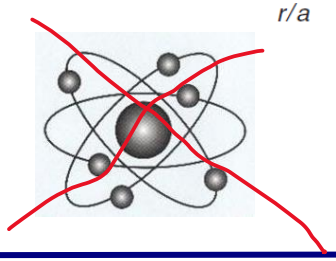
$$R_{10}(r) = R_{1s}(r) = \left(\frac{Z}{a}\right)^{3/2} 2\, e^{-Zr/a}$$

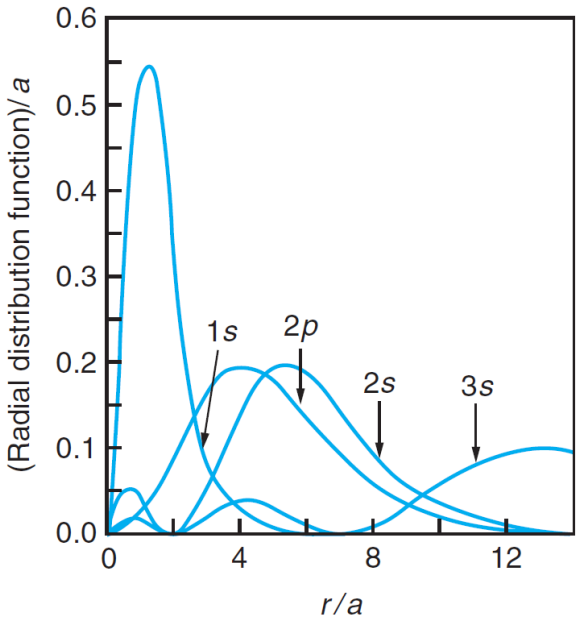
$$R_{20}(r) = R_{2s}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$R_{21}(r) = R_{2p}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}$$



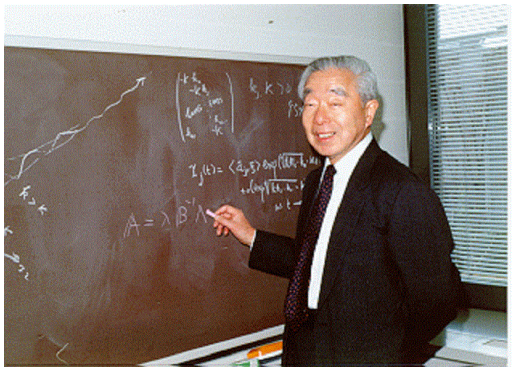


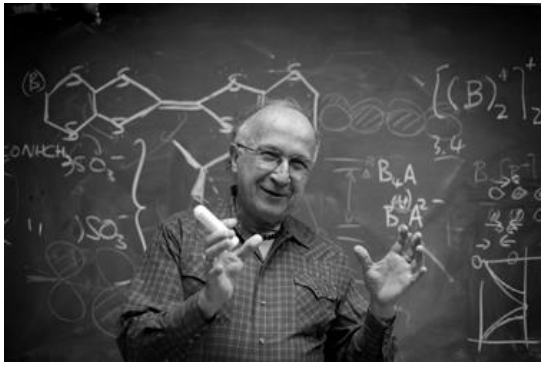




Orbitaller

1981 Nobel Kimya Ödülü, Fukui & Hoffmann





R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.* **87**, 395 (1965). See also R. Hoffmann, *Angew. Chem. Int. Ed.* **43**, 2, 2004, for historical insights.

R. B. Woodward and R. Hoffmann, *The Conservation of Orbital Symmetry*. Academic Press, New York, 1970.

14-9 Qualitative Molecular Orbital Theory of Reactions

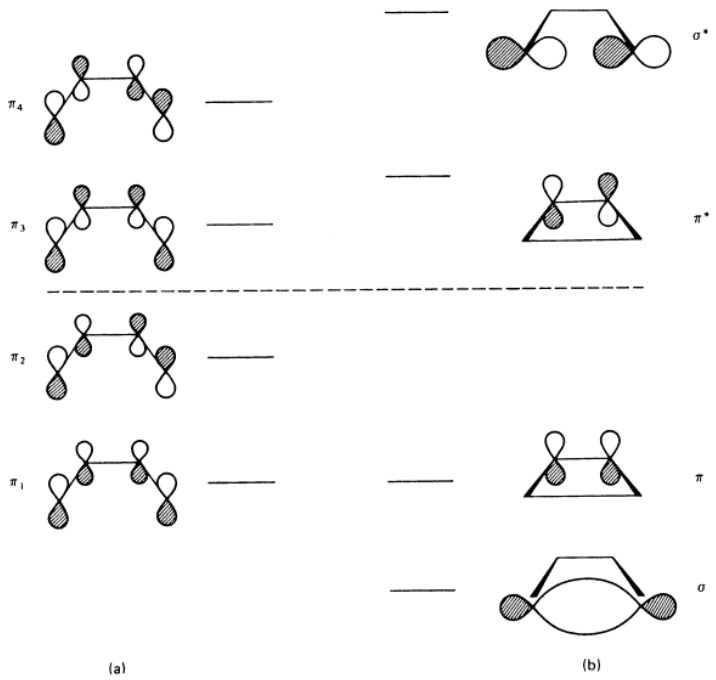


Figure 14-20 ▶ MOs associated with bonds being broken or formed in the electrocyclic closure of (a) *cis*-1,3-butadiene to (b) cyclobutene.

Yüksek başarımlı hesaplama sistemleri (Süper bilgisayarlar) kullanarak kimyasal yapıya, yani elektronların davranışına dair merak ettiklerimizi (enerji, reaktivite, spektroskopik özellikler, vb.) Schrödinger denkleminin yaklaşık çözümleri ile öğreniyoruz.

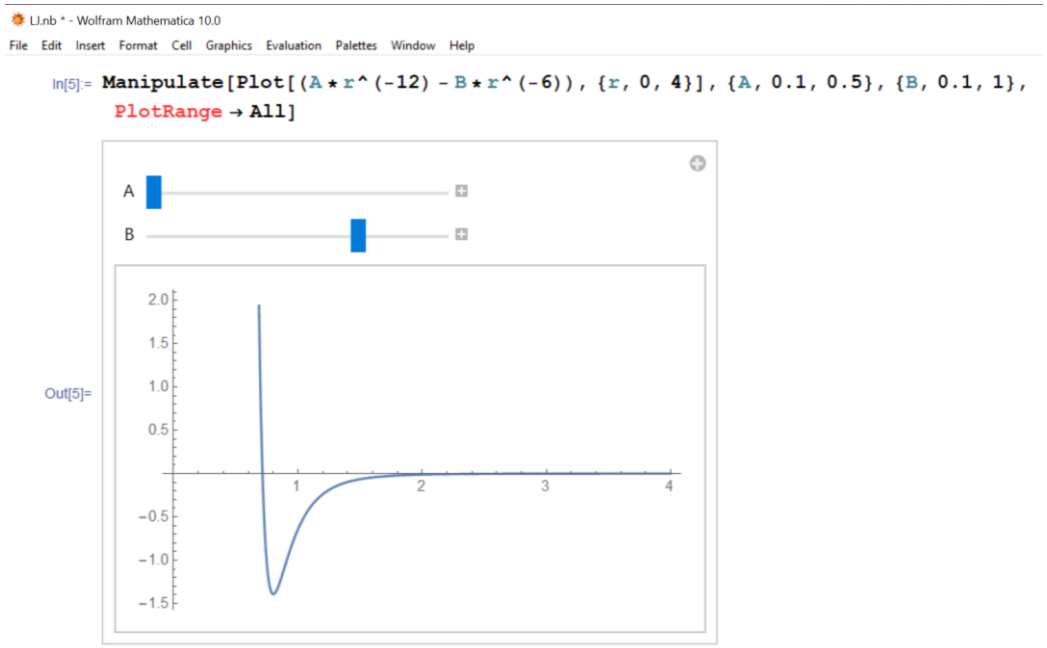
“Hesaplamalı kimya”

“Kimyanın önemli bir kısmını matematiksel hesap ile yapacağımız zamanlardan çok uzak olmasak gerek.”
Joseph Louis Gay-Lussac (1808)

Neden küçük molekül?

Aktivasyon nedir?

O_2, CH_4, H_2O



Ruedenberg: "Diatomic molecules are peculiar because they only have two ends, and these ends are very close together."

Coulson, C. A. ***Reviews of Modern Physics*** **1960**, *32*, 170.

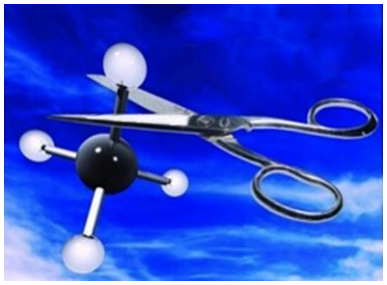
Aktivasyon ne işe yarayacak?

O_2, CH_4, H_2O, H_2, CO_2, N_2 … SO_x, NO_x …

- ✓ **Fosil yakıtları**
- ✓ **Yenilenebilir enerji**
- ✓ **Yapay fotosentez**

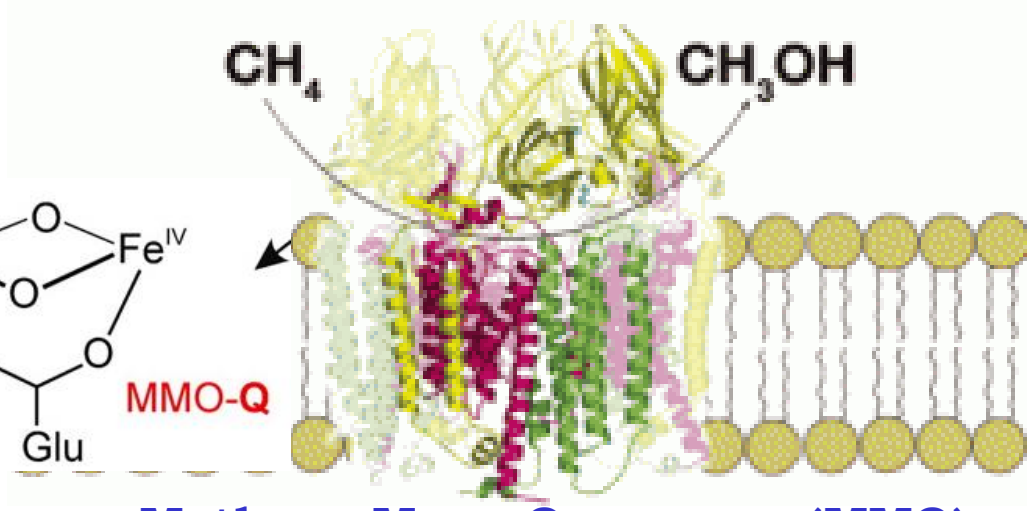
*** Biyolojik ve katalitik sistemler**

Küçük Molekül Aktivasyonu



104 kcal/mol
KAPALI KABUK
SİNGLET

118 kcal/mol
KARARLI TRİPLET
BİRADİKAL

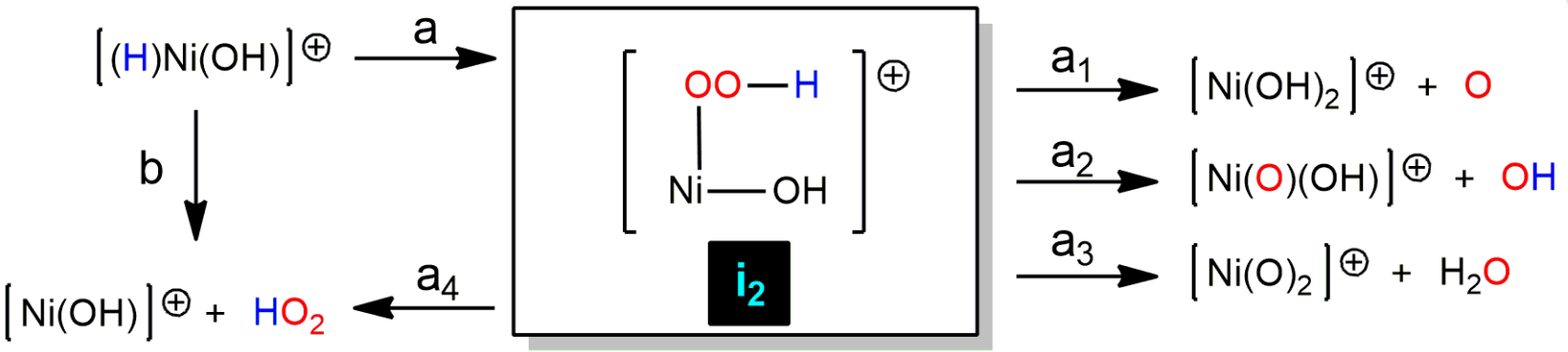


Methane Mono Oxygenase (MMO)

MMO gibi bir aktivatör var mı?

$[(H)Ni(OH)]^+$

Metan ve oksijeni aktive eden en küçük sistem.



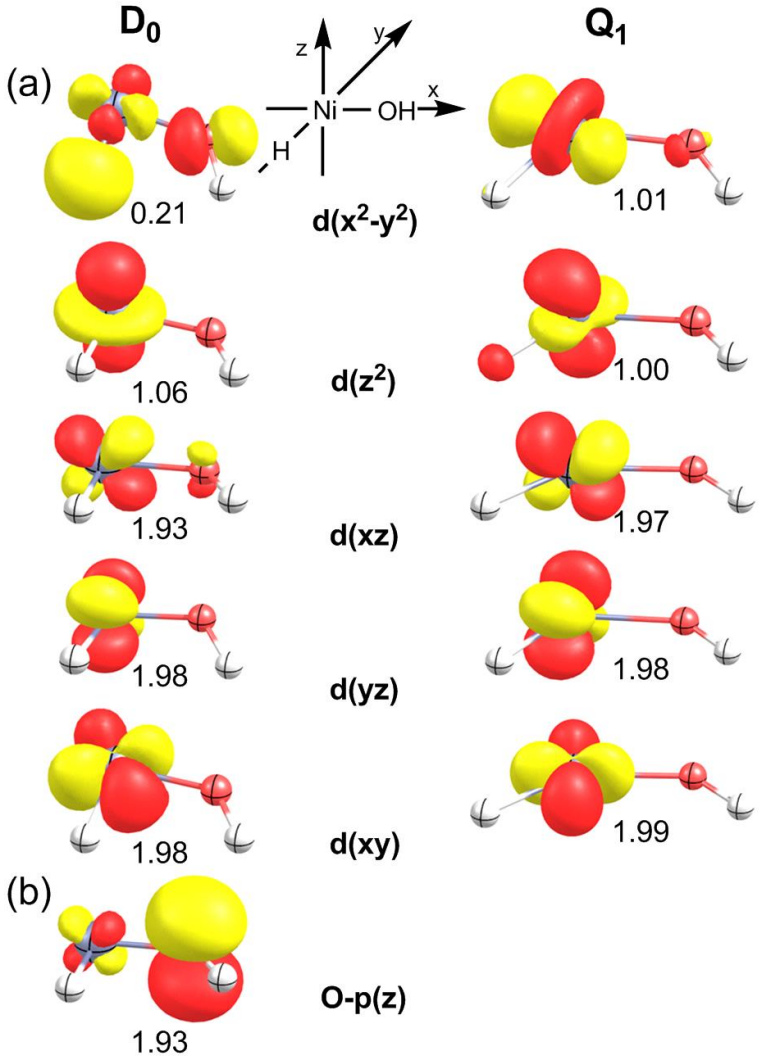
$[(HO)NiOOH]^+$ kritik ara ürün.

$[(H)Ni(OH)]^+$ neden özel?
$[(HOO)Ni(OH)]^+$ nasıl oluşuyor?

"Two-State Reactivity in Organometallic Gas-Phase Ion Chemistry", Shaik S.; Danovich D.; Fiedler A.; Schröder D.; Schwarz. H., *Helv. Chim Acta,* 1995, 78, 1393-1407. "Insertion of Molecular Oxygen in Transition-Metal Hydride Bonds, Oxygen- Bond Activation, and Unimolecular Dissociation of Metal Hydroperoxide Intermediates" Schlangen, M.; Schwarz, H., *Helv. Chim. Acta,* 2008, *91*, 379-386.

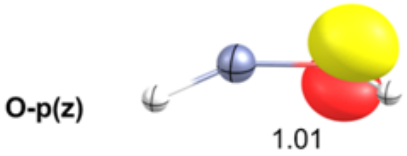
Teşekkür: Prof. Helmut Schwarz@*TU Berlin*

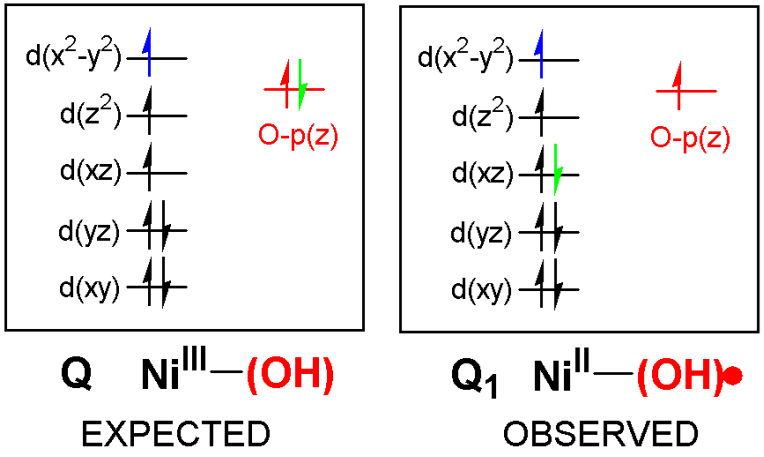
[(H)Ni(OH)]$^{+}$, elektronlar ne yapıyor?



Temel dublet (D_0) ve uyarılmış kuartet (Q_1)

~25 kcal mol^{-1}

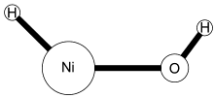


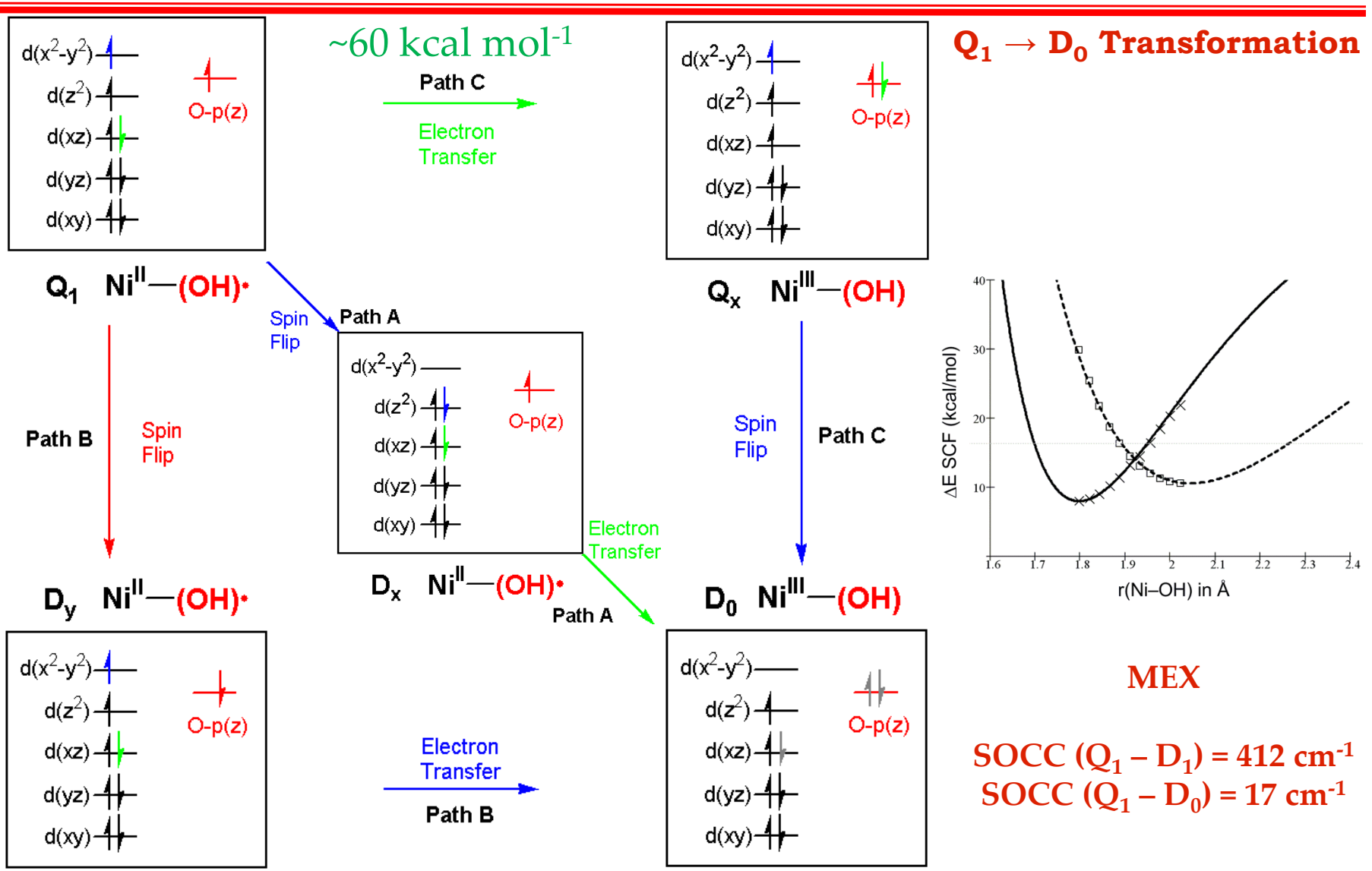


OH redox-noninnocent

Irigoras, A.; Elizalde, O.; Silanes, I.; Fowler, J. E.; Ugalde, J. M., *J. Am. Chem. Soc.* **2000,** 122, (1), 114-122.

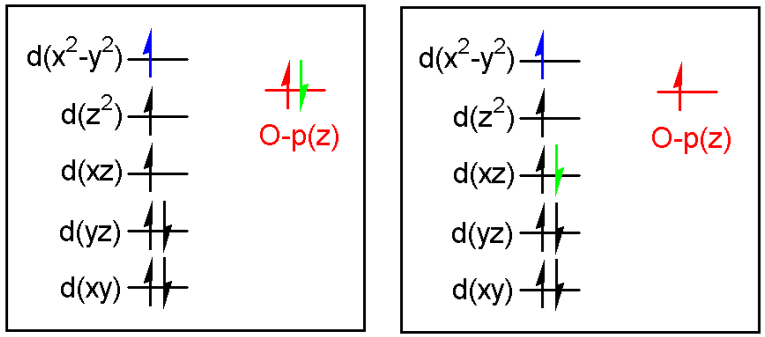
[(H)Ni(OH)]$^+$, elektronlar ne yapıyor?





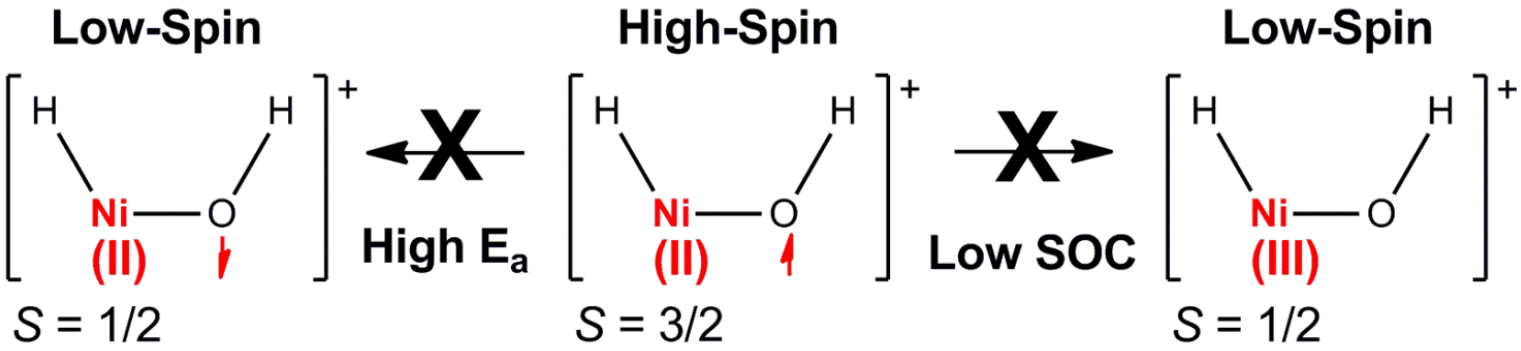
Y. Dede, X. Zhang, M. Schlangen, H. Schwarz, M. H. Baik, *J. Am. Chem. Soc.* **2009**, *131*, 12634-12642

$[(H)Ni(OH)]^+$

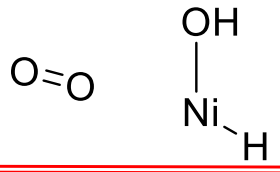


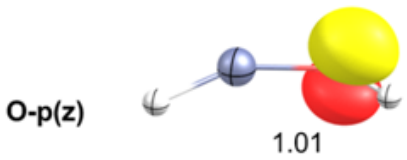
Q Ni^{III}—(OH) EXPECTED

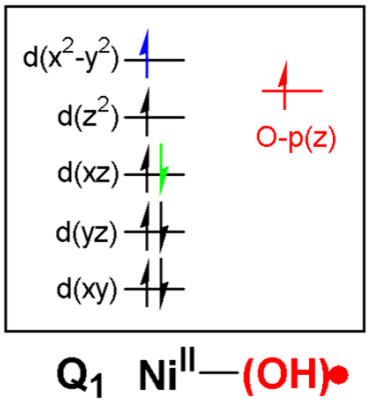
Q_1 Ni^{II}—(OH)• OBSERVED



Y. Dede, X. Zhang, M. Schlangen, H. Schwarz, M. H. Baik, *J. Am. Chem. Soc.* **2009**, *131*, 12634-12642







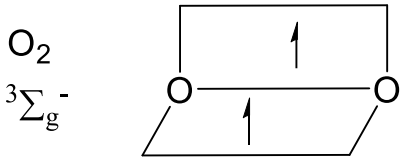
[(H)Ni(OH)]$^+$ neden özel?

[(HOO)Ni(OH)]$^+$nasıl oluşur?

Radikal merkez ile (O, p_z(↑)) reaktivite arasındaki ilişki nedir?

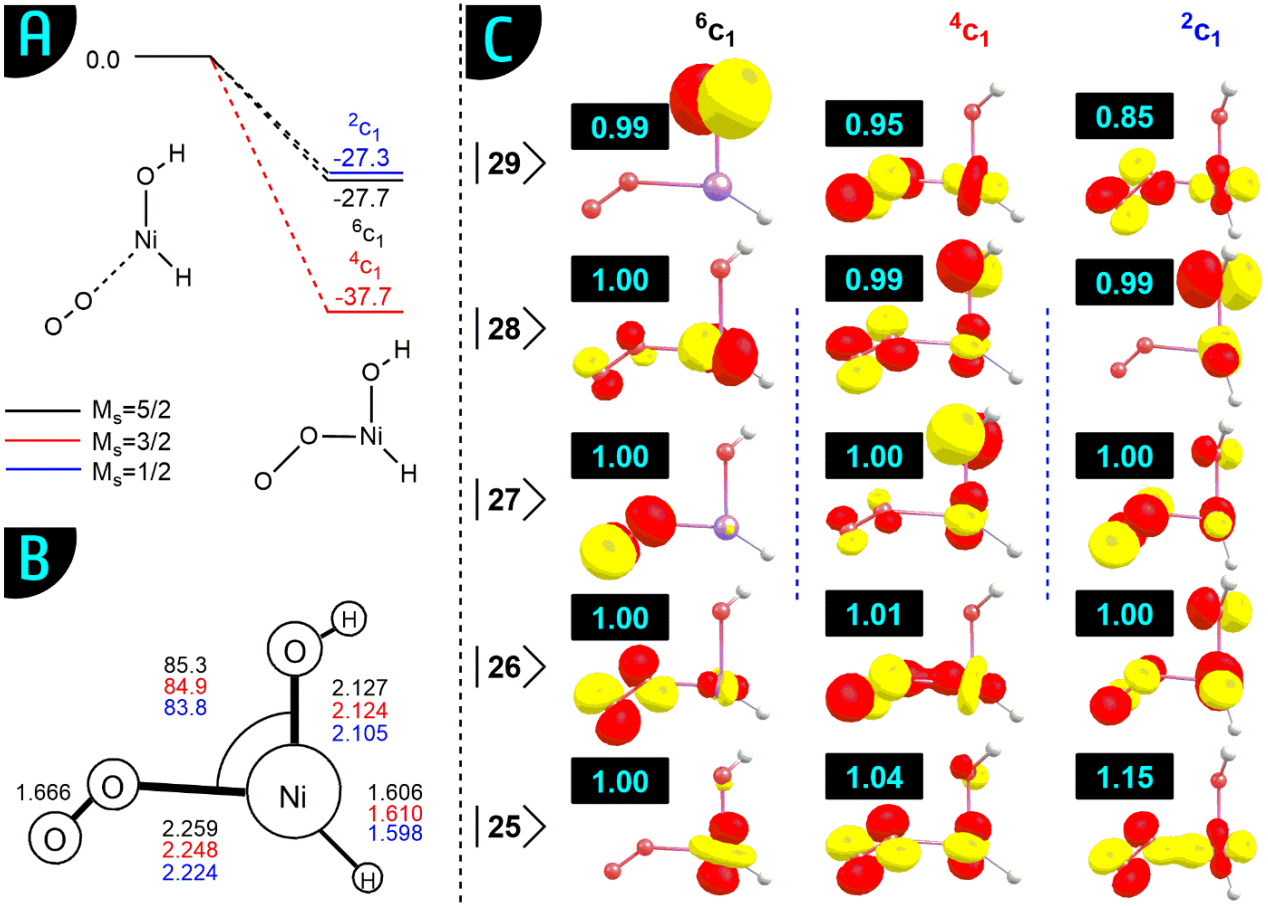
Bir başka deyişle;

Radikal aktivatör (dört-atomlu) radikal substratı (iki atomlu) nasıl aktive eder?



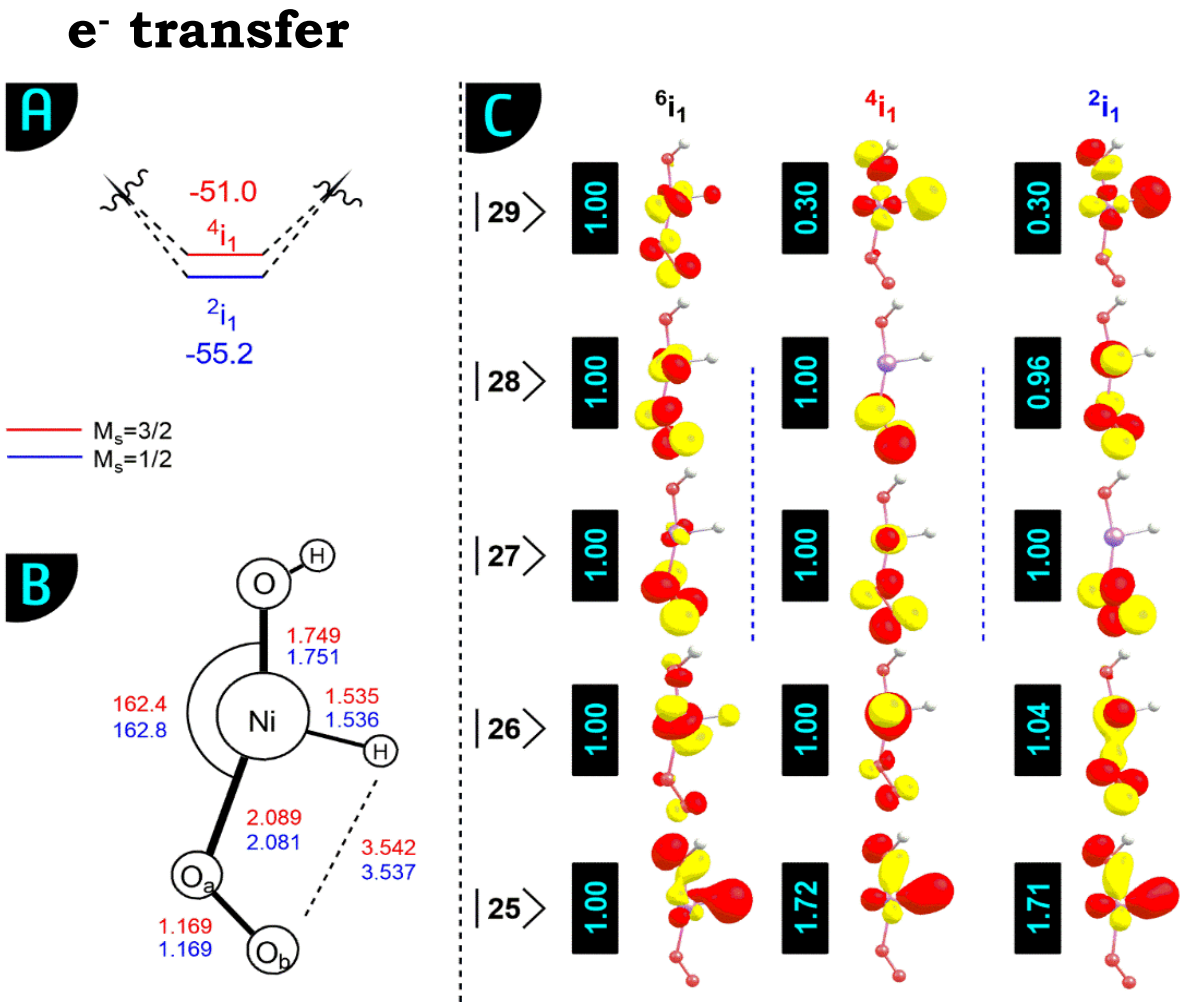
O_2 + [Ni(H)(OH)]$^+$

Başlangıç Kompleksi



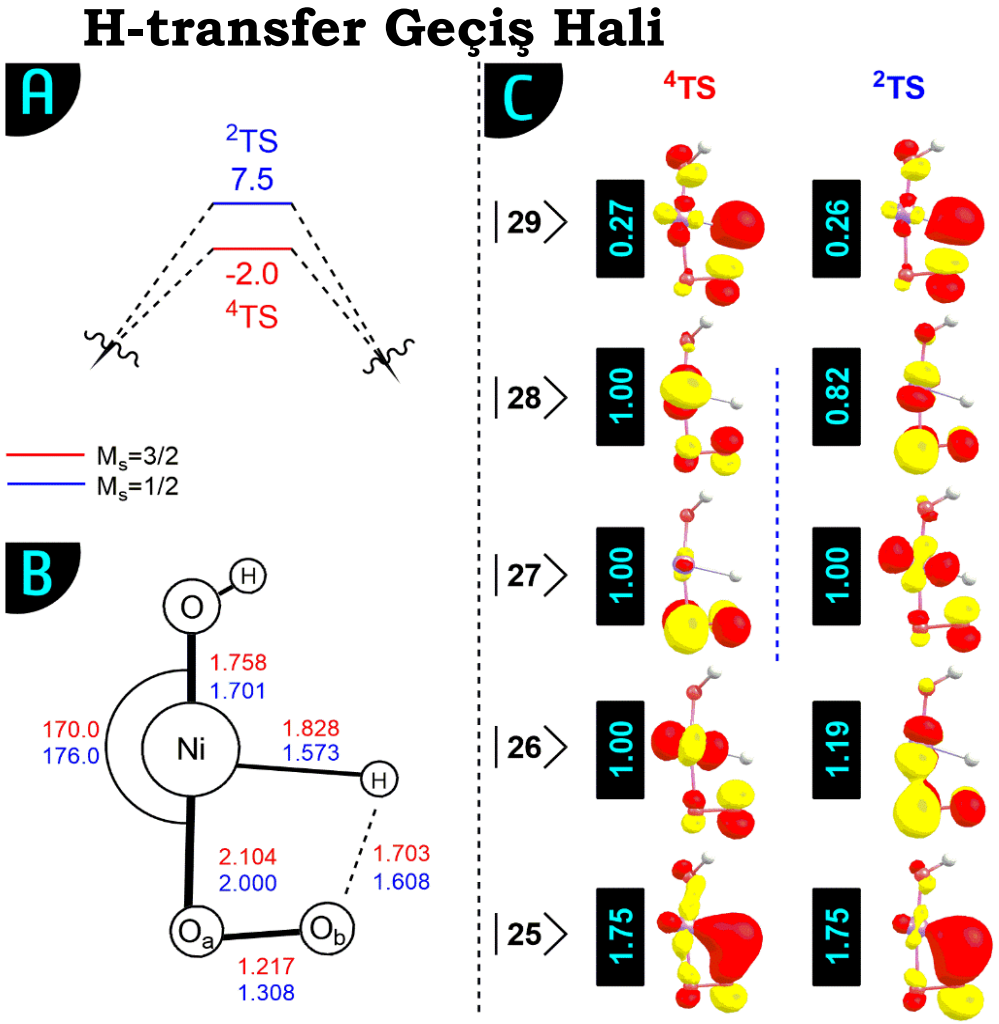
Relative energies (kcal·mol^{-1}) (a) selected geometric parameters (b) natural orbital occupancy numbers and natural orbital plots

O_2 + [Ni(H)(OH)]$^+$



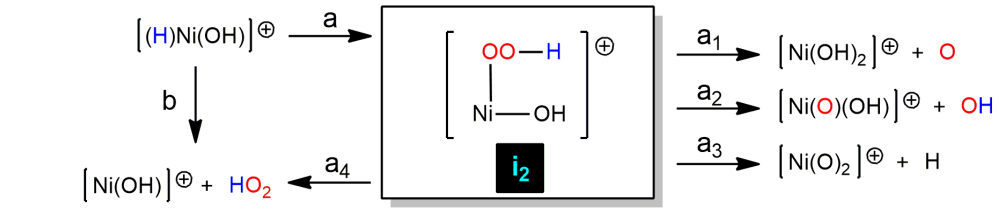
Relative energies (kcal·mol^{-1}) (a) selected geometric parameters (b) natural orbital occupancy numbers and natural orbital plots (c)

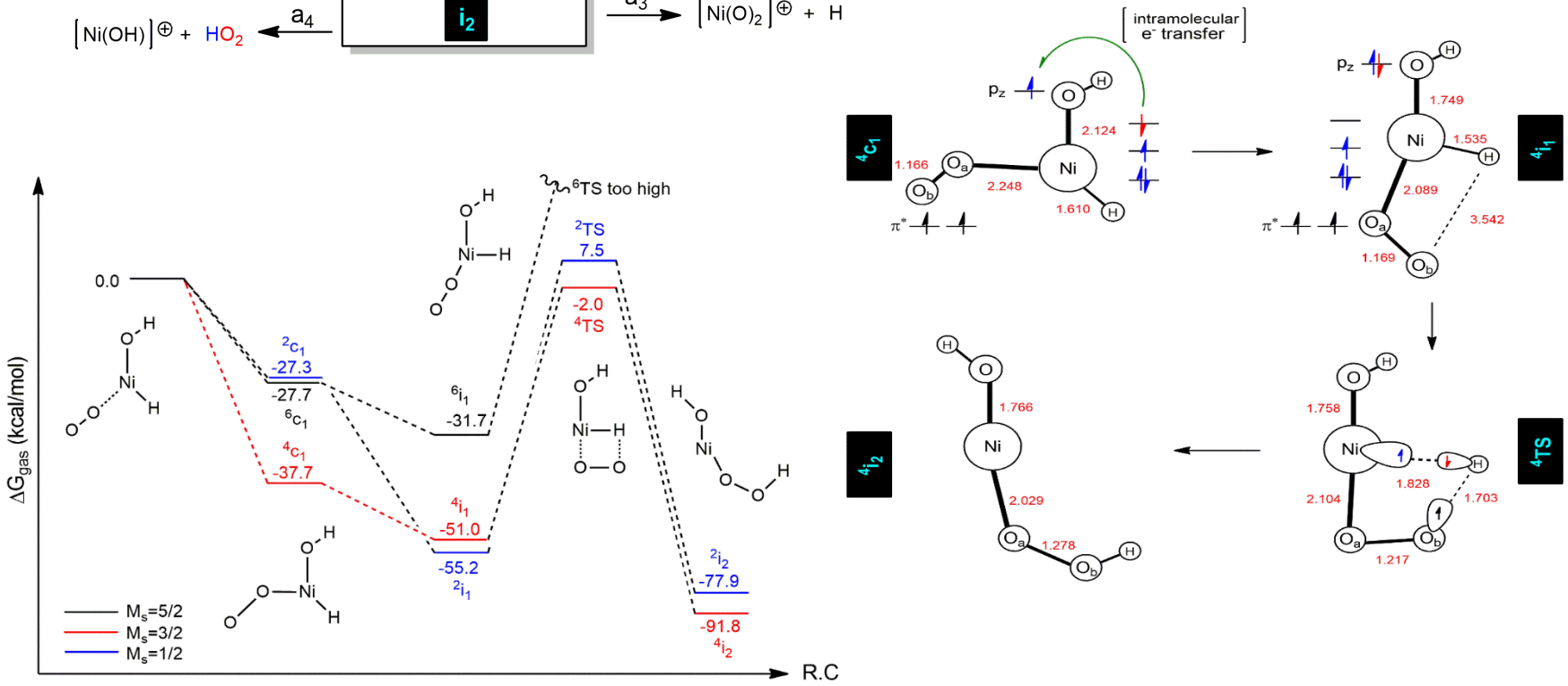
O_2 + [Ni(H)(OH)]$^+$



Relative energies (kcal·mol^{-1}) (a) selected geometric parameters (b) natural orbital occupancy numbers and natural orbital plots (c)

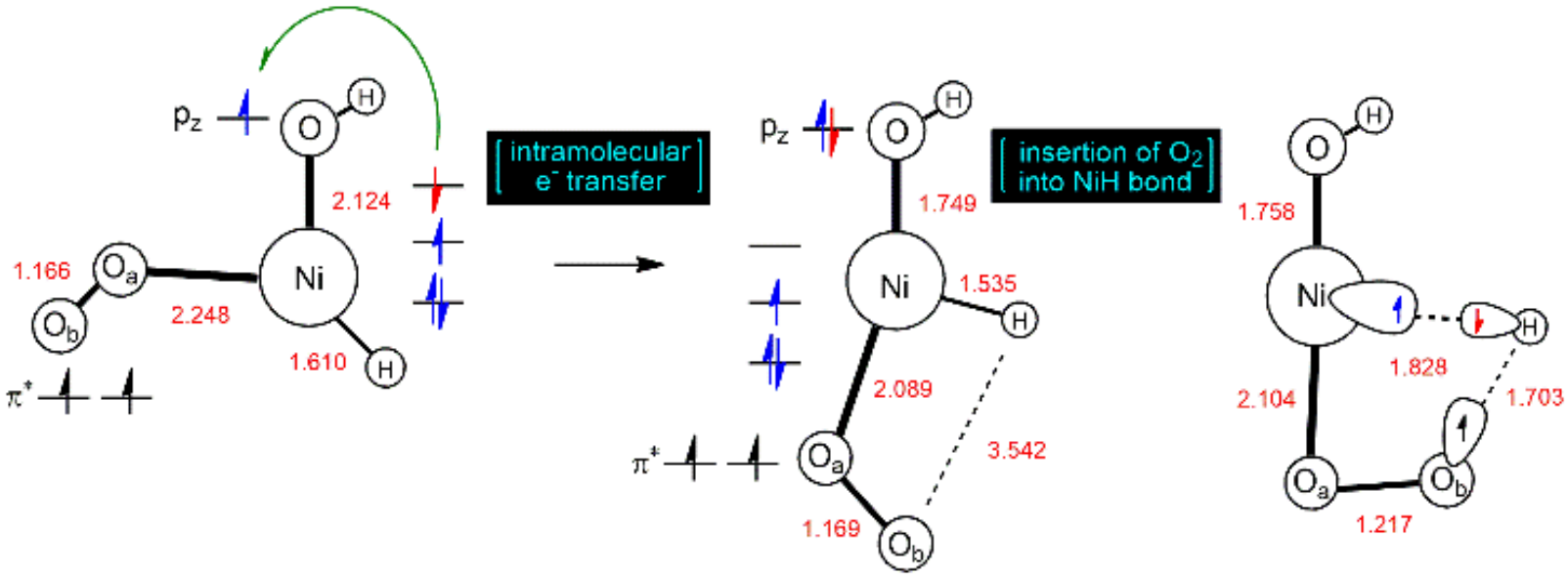
O_2 + $[Ni(H)(OH)]^+$





CCSD(T)/def2-TZVP energies (kcal·mol^{-1})

O_2 + [Ni(H)(OH)]$^+$



RADİKALİN RADİKAL İLE AKTİVASYONU TERMAL!

Aktivasyon ne işe yarayacak?

O_2, CH_4, H_2O, H_2, CO_2, N_2 … SO_x, NO_x …

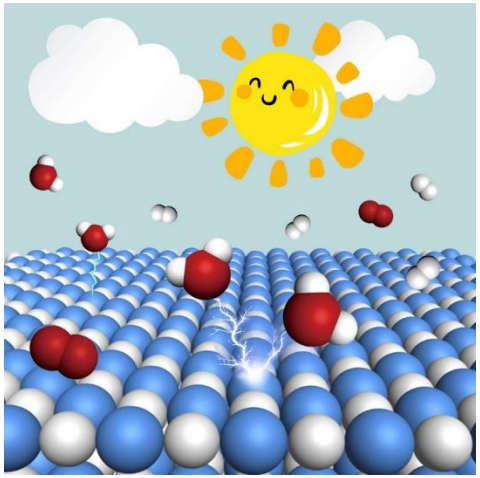
- ✓ **Fosil yakıtları**
- ✓ **Yenilenebilir enerji**
- ✓ **Yapay fotosentez**

*** Biyolojik ve katalitik sistemler**

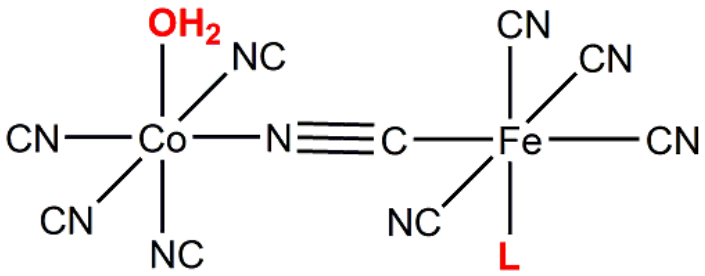
Suyun aktivasyonu, oksidasyonu, parçalanması

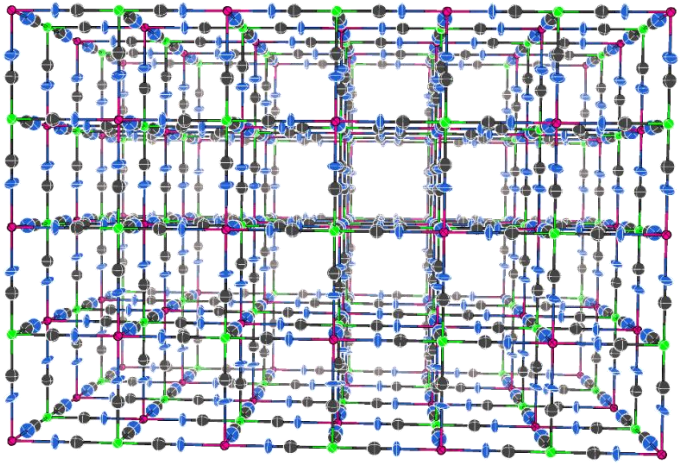
$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$

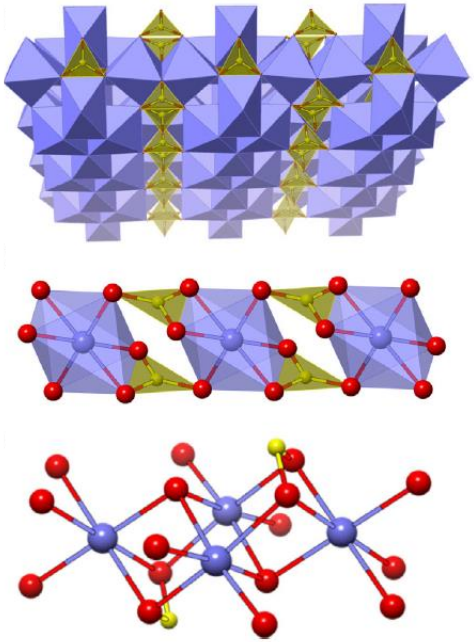
E° = 1.23 V vs (NHE) at pH 0.0 (1 M H^+)



Su Aktivasyonu/Su oksidasyon katalizörü (WOC)





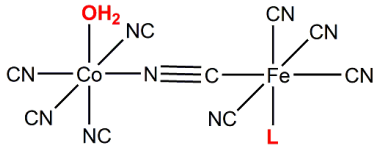


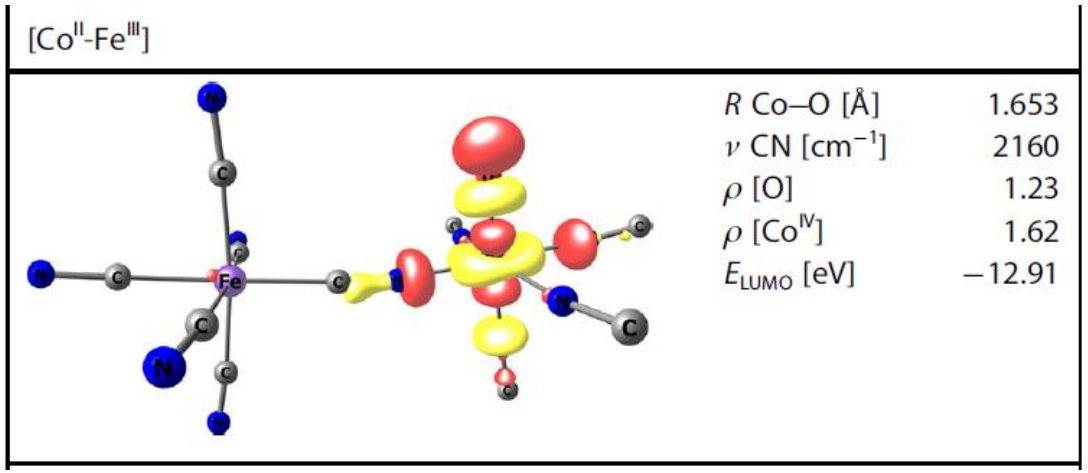
Prusya mavisi

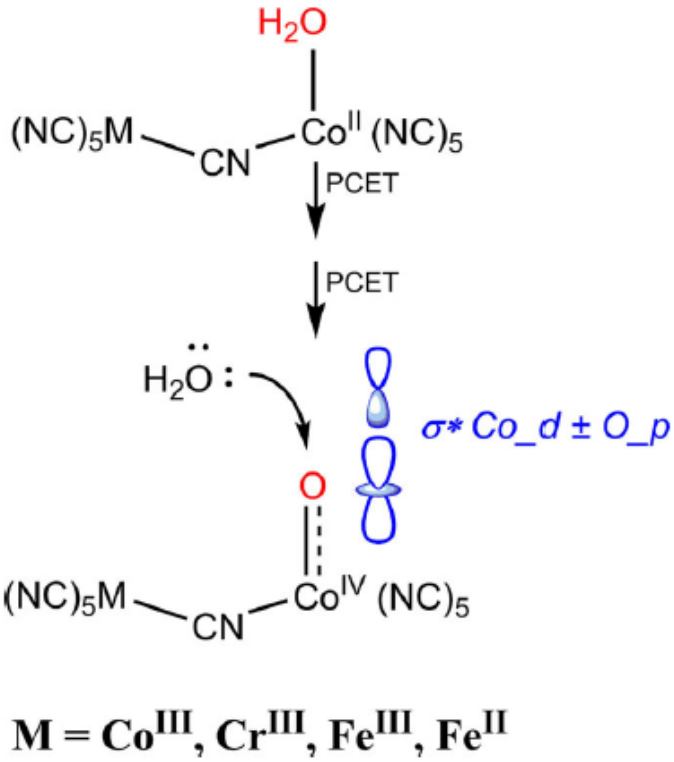
Kobalt Borat

Teşekkür: Dr. Ferdi Karadaş *@Bilkent Üniv.-FF-Kimya*

O–O Bağ Oluşumu







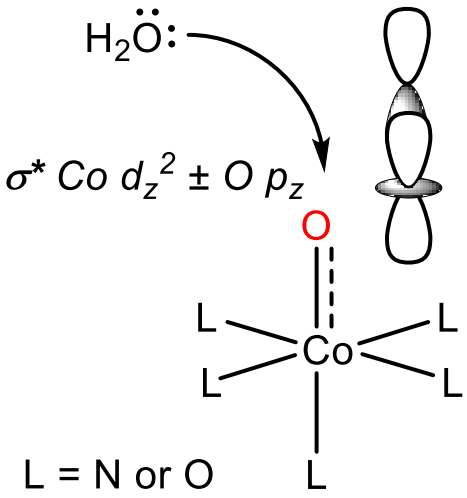
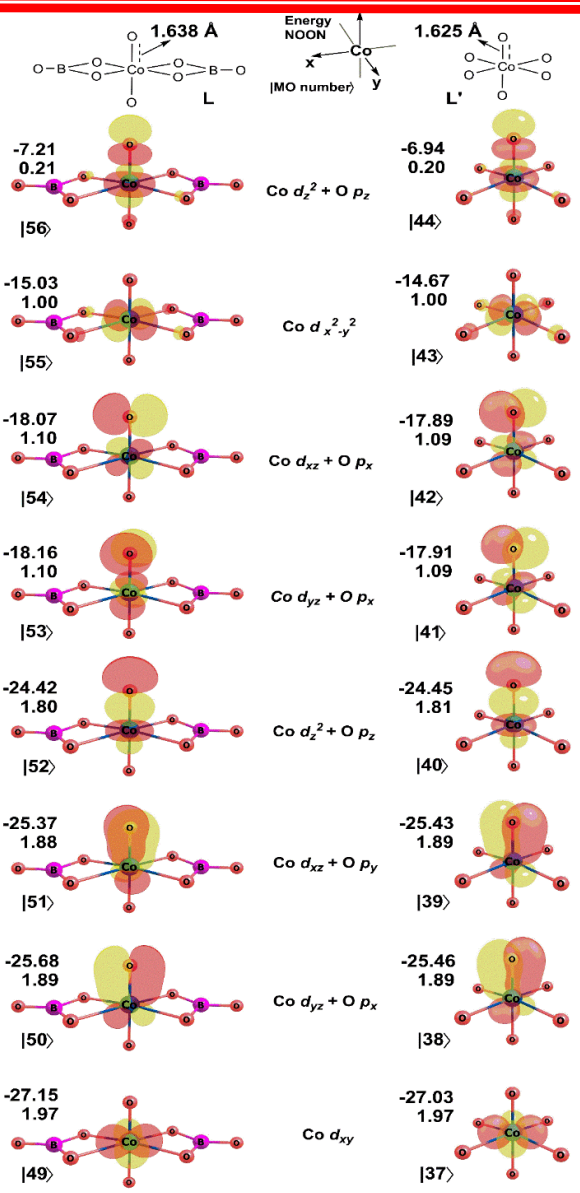
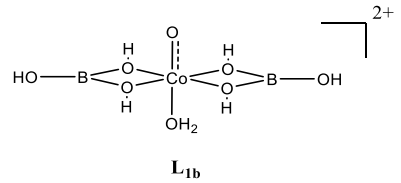


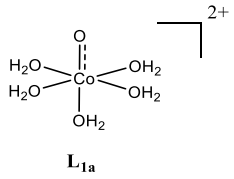
Figure 8. O–O bond formation at the Co^{IV}–O center.

O–O Bağ Oluşumu

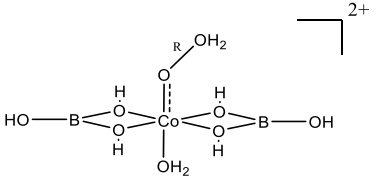




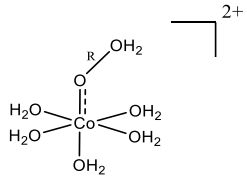
L_{1b}



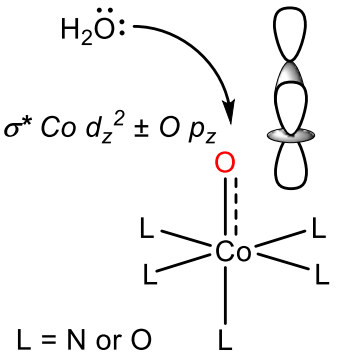
L_{1a}

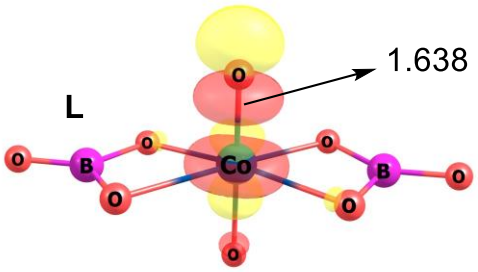


L_{3b}



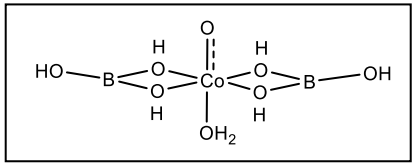
L_{3a}

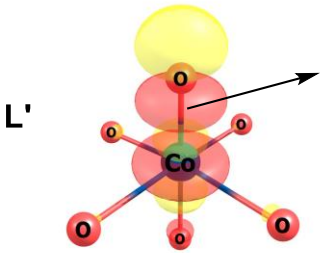




E_{LUMO}= -7.21

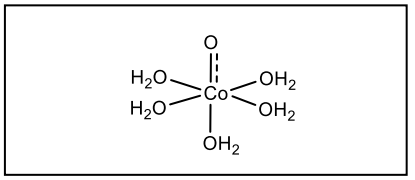
NOON=0.21



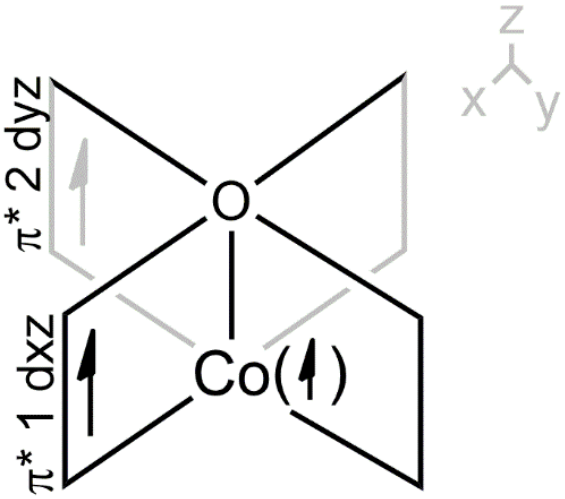


E_{LUMO}=-6.94

NOON=0.20



Co–O merkezi neden özel?



ELSEVIER

Journal of Molecular Structure (Theochem) 424 (1998) 1–6

THEO CHEM

Viewpoint paper

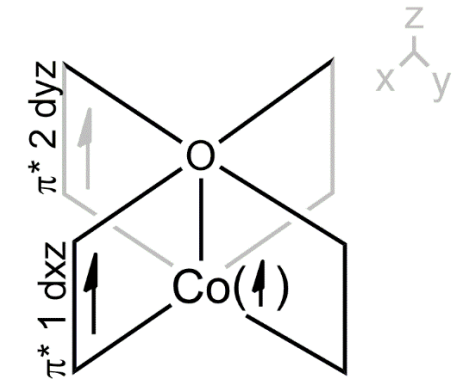
Qualitative thinking in the age of modern computational chemistry—or what Lionel Salem knows[1]

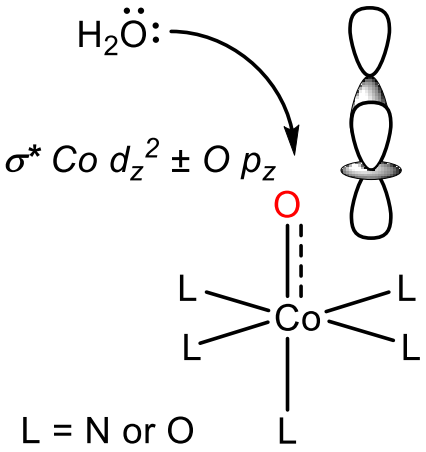
Roald Hoffmann

LIONEL SALEM

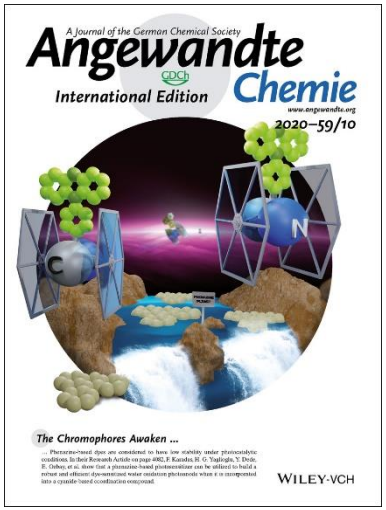
Electrons in Chemical Reactions

Co–O Merkezi





|Co(d)(↑)> |Co(d)±O(p)(↑)> |Co(d)±O(p)(↑)>
(S = 3/2)



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İlgililere kaynak önerileri:

Hesaplamalı kimyaya giriş için kısa bir okuma listesi:

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Başlangıç için faydalı bir web sitesi:

http://linux4chemistry.info/2013/index.html

TEŞEKKÜR

BİLİM AKADEMİSİ

TÜBA

GÜ-BAP (05/2016-02)

TRUBA - HPC

TÜBİTAK
110T647
212T047
114Z790
117Z337

TEŞEKKÜR: http://w3.gazi.edu.tr/~dede/pages/people.html

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