Application of the Coulomb spheroidal basis for diatomic molecular calculations

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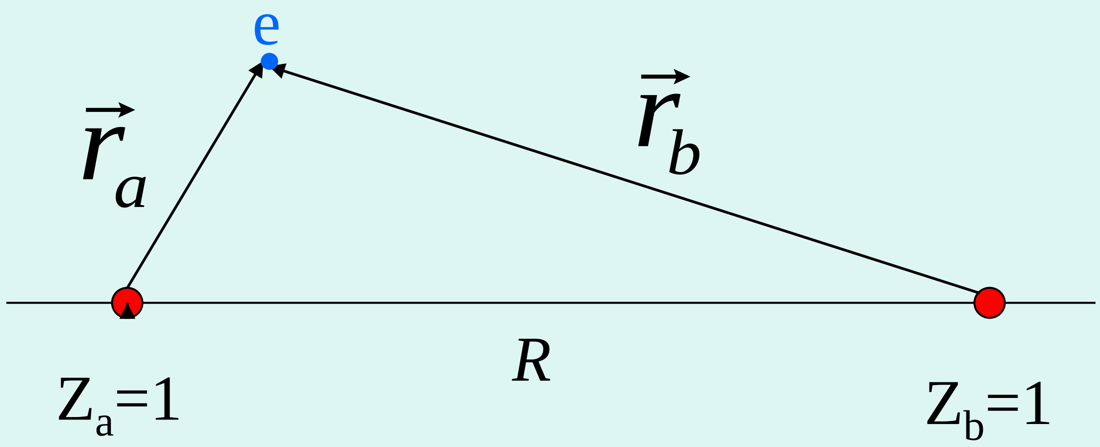
SYMMETRICAL DIATOMIC MOLECULES

$$H_2^+,\ H_2,\ C_2,\ N_2,\ O_2$$

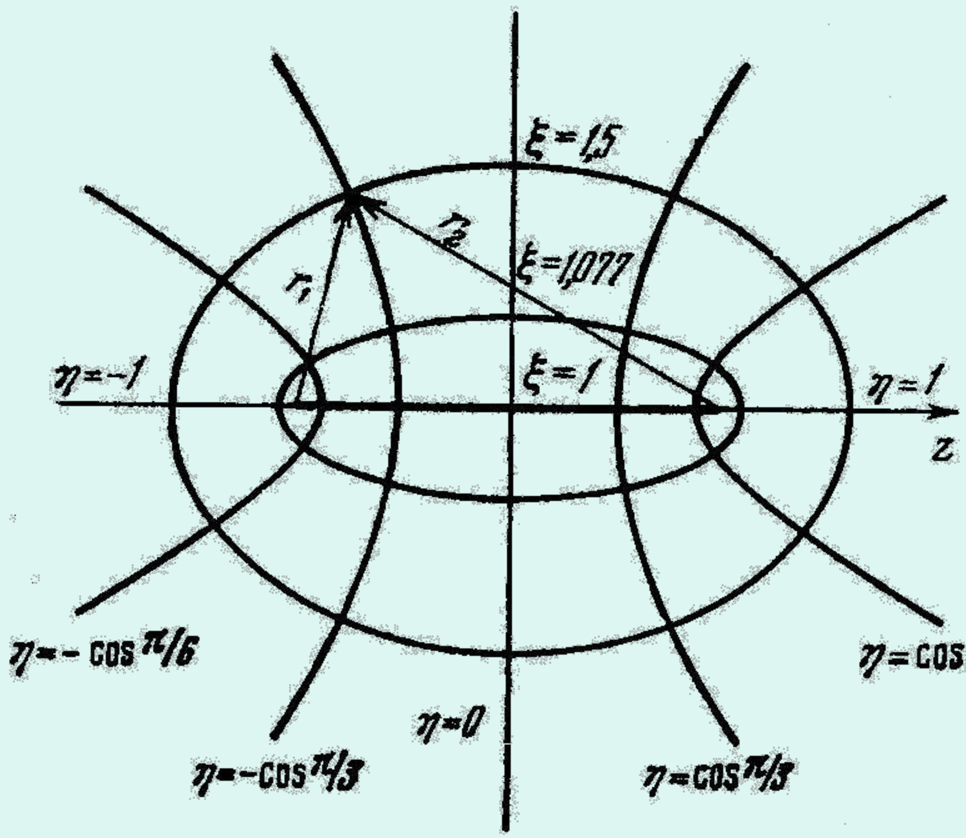
Heitler and London (LCAO)

Hund and Mulliken

Hydrogen molecular ion H_2^+



Prolate spheroidal coordinate system



$$\xi = \frac{r_a + r_b}{R}, \quad \eta = \frac{r_a - r_b}{R}, \quad \varphi = arctg(y/x)$$

$$1 \le \xi < \infty, \quad -1 \le \eta \le 1 \quad 0 \le \varphi < 2\pi$$

Schrödinger equation for hydrogen molecular ion

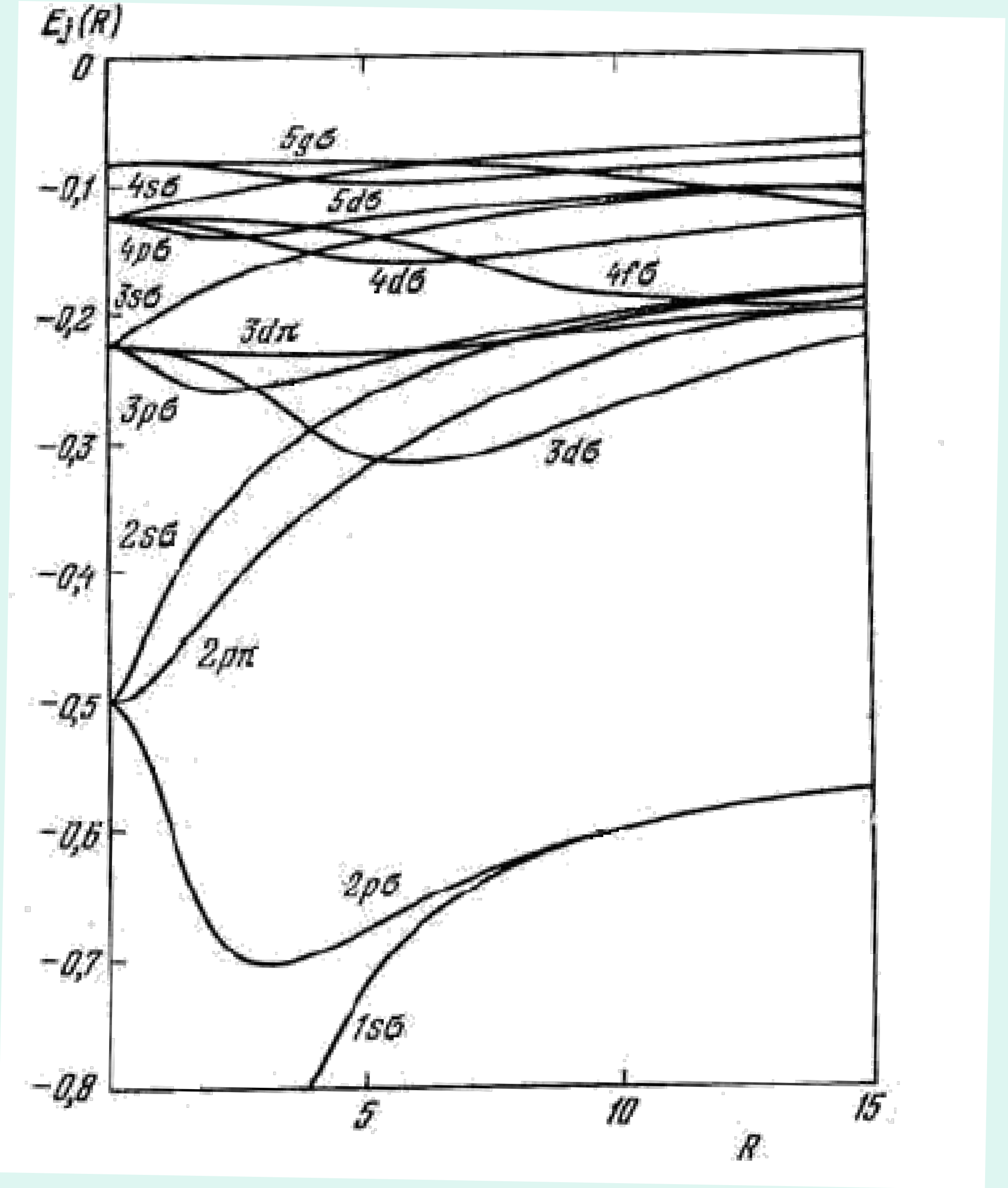
$$\left(-\frac{1}{2}\Delta-\frac{1}{r_a}-\frac{1}{r_b}\right)\Psi^{(\pm)}=\varepsilon^{(\pm)}(R)\Psi^{(\pm)}$$

$$\Psi^{(\pm)}_{n_\xi n_\eta m}=X_{n_\xi m}(\xi,R)Y^{(\pm)}_{n_\eta m}(\eta,R)\frac{e^{-im\varphi}}{\sqrt{2\pi}}$$

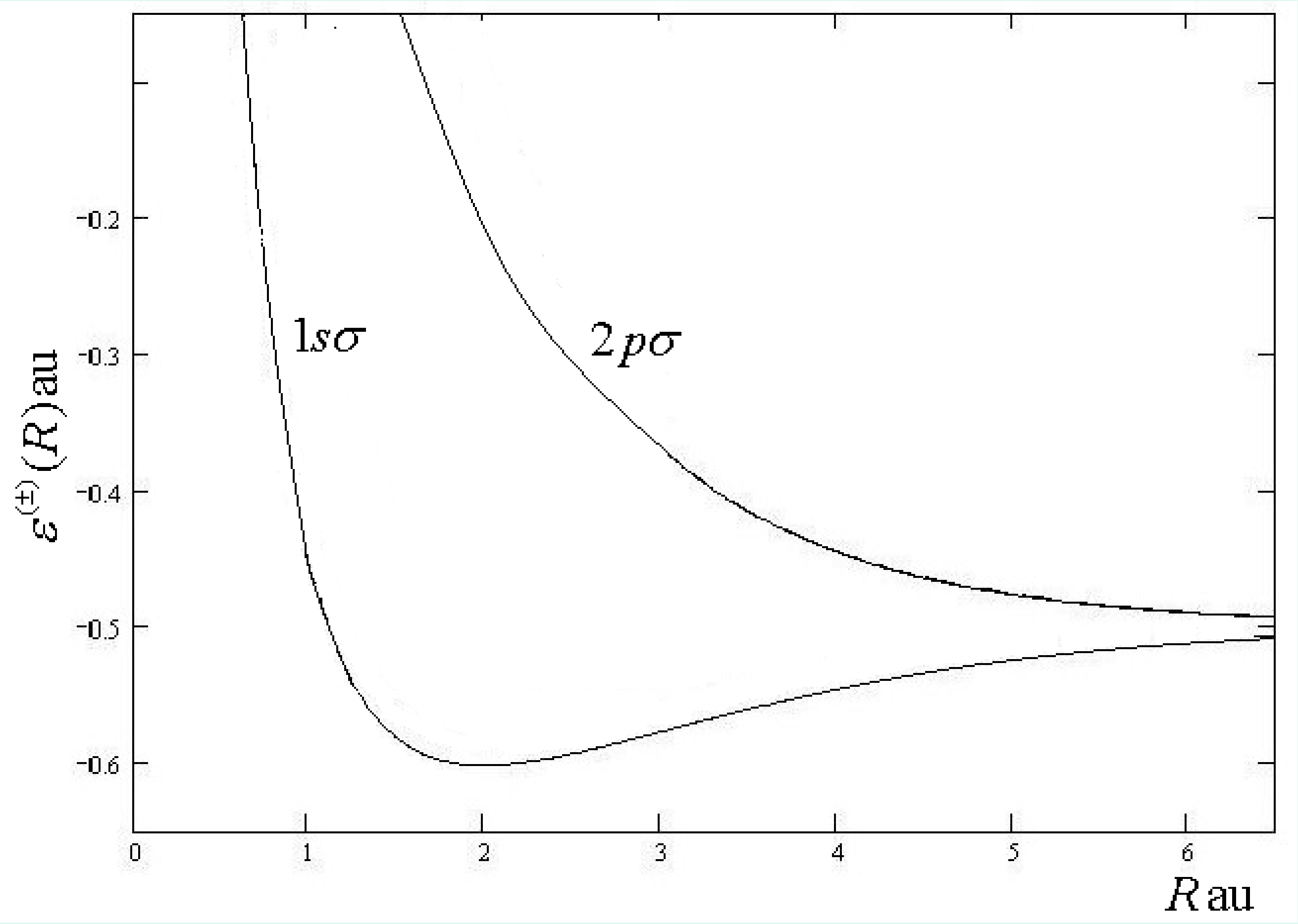
$$\frac{d}{d\xi}\left(\xi^2-1\right)\frac{dX}{d\xi}+\left[\lambda+\frac{\varepsilon^{(\pm)}R^2}{2}\xi^2+2R\xi-\frac{m^2}{\xi^2-1}\right]X(\xi,R)=0$$

$$\frac{d}{d\eta}\left(1-\eta^2\right)\frac{dY^{(\pm)}}{d\eta}+\left[-\lambda-\frac{\varepsilon^{(\pm)}R^2}{2}\eta^2-\frac{m^2}{1-\eta^2}\right]Y^{(\pm)}(\eta,R)=0$$

Electornic energies of H_2^+



The ground and first excited terms of H_2^+



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Schrödinger equation for hydrogen-like ion

$$\left(-\frac{1}{2}\Delta-\frac{Z_{a,b}}{r_{a,b}}\right)\Psi^{a,b}=\varepsilon^{a,b}(R)\Psi^{a,b}$$

$$\Psi^{a,b}_{n_\xi n_\eta m}=X_{n_\xi m}(\xi,R)Y^{a,b}_{n_\eta m}(\eta,R)\frac{e^{-im\varphi}}{\sqrt{2\pi}}$$

$$\frac{d}{d\xi}\left(\xi^2-1\right)\frac{dX}{d\xi}+\left[\lambda+\frac{\varepsilon R^2}{2}\xi^2+ZR\xi-\frac{m^2}{\xi^2-1}\right]X(\xi,R)=0$$

$$\frac{d}{d\eta}\left(1-\eta^2\right)\frac{dY^{a,b}}{d\eta}+\left[-\lambda-\frac{\varepsilon R^2}{2}\eta^2\mp ZR\eta-\frac{m^2}{1-\eta^2}\right]Y^{a,b}(\eta,R)=0$$

$$n=n_\xi+n_\eta+m+1$$

The Coulomb spheroidal wave functions

1□ $n = m + 1, \; n_\xi + n_\eta = 0;$

$$X_{0m} = e^{-ZR\xi/2n} W(\xi)$$

$$Y_{0m}^{a,b} = e^{\mp ZR\eta/2n} W(\eta)$$

2□ $n = m + 2, \; n_\xi + n_\eta = 1, 2;$

$$X_{0m,1m} = e^{-ZR\xi/2n} \left(\xi - \frac{nh_{1,2}}{ZR} \right) W(\xi)$$

$$Y_{1m,0m}^{a,b} = e^{\mp ZR\eta/2n} \left(\eta \mp \frac{nh_{1,2}}{ZR} \right) W(\eta)$$

3□ $n = m + 3, \quad n_\xi + n_\eta = 1, 2, 3;$

$$X_{0m,1m,2m} = e^{-ZR\xi/2n}\left(\xi^2 - \frac{nh_{1,2,3}}{ZR}\xi + \frac{n^2 h_{1,2,3}}{2Z^2R^2}(h_{1,2,3} - 2m - 4) - 1\right)W(\xi)$$

$$Y^{a,b}_{2m,1m,0m} = e^{\mp ZR\eta/2n}\left(\eta^2 \mp \frac{nh_{1,2,3}}{ZR}\eta + \frac{n^2 h_{1,2,3}}{2Z^2R^2}(h_{1,2,3} - 2m - 4) - 1\right)W(\eta)$$

$$W(\xi) = (\xi^2 - 1)^{m/2} \qquad W(\eta) = (1 - \eta^2)^{m/2}$$

$$n = n_\xi + n_\eta + m + 1$$

The basic equations

$$\left\{ X_{nn_\xi m}(\xi, R) Y^{a}_{nn_\eta m}(\eta, R) e^{-im\varphi} \right\}$$

$$\left\{ X_{nn_\xi m}(\xi, R) Y^{a}_{nn_\eta m}(\eta, R) e^{-im\varphi} \right\}$$

$$Y^{(\pm)}_{nn_\eta m} = Y^{a}_{nn_\eta m}(\eta, R) \pm Y^{b}_{nn_\eta m}(\eta, R)$$

$$\Psi^{(\pm)}(\xi, \eta, \varphi, R) = \Phi^{(\pm)}(\xi, \eta, R) e^{im\varphi}$$

$$\Phi^{(\pm)} = \sum_{n=1}^{\infty} \sum_{n_\eta=0}^{n-m-1} C^{(\pm)}_{nn_\eta m}(R) X_{nn_\xi m}(\xi, R) Y^{(\pm)}_{nn_\eta m}(\eta, R)$$

The basic equations

$$\sum_{n=1}^{\infty}\sum_{n_\eta=0}^{n-m-1}\left[\left(\varepsilon^{(\pm)}-E_n\right)U^{(\pm)}_{n\square n_\eta\square,nn_\eta}+V^{(\pm)}_{n\square n_\eta\square,nn_\eta}\right]C^{(\pm)}_{nn_\eta}=0$$

$$\left|\left(\varepsilon^{(\pm)}-E_n\right)U^{(\pm)}_{n\square n_\eta\square,nn_\eta}+V^{(\pm)}_{n\square n_\eta\square,nn_\eta}\right|=0$$

$$U^{(\pm)}_{n\square n_\eta\square,n\,n_\eta}=\langle X_{n\square n_\xi\square}\left|\xi^2\right|X_{nn_\xi}\rangle\langle\Upsilon^{(\pm)}_{n\square n_\eta\square}\left|\Upsilon^{(\pm)}_{nn_\eta}\right.\rangle-\langle X_{n\square n_\xi\square}\left|X_{nn_\xi}\right.\rangle\langle\Upsilon^{(\pm)}_{n\square n_\eta\square}\left|\eta^2\right|\Upsilon^{(\pm)}_{nn_\eta}\rangle$$

$$V^{(\pm)}_{n\square n_\eta\square,n\,n_\eta}=\frac{2}{R}\Big[(2-Z)\langle X_{n\square n_\xi\square}\left|\xi\right|X_{nn_\xi}\rangle\langle\Upsilon^{(\pm)}_{n\square n_\eta\square}\left|\Upsilon^{(\pm)}_{nn_\eta}\right.\rangle$$

$$+Z\langle X_{n\square n_\xi\square}\left|X_{nn_\xi}\right.\rangle\langle\Upsilon^{(\pm)}_{n\square n_\eta\square}\left|\eta\right|\Upsilon^{(\mp)}_{nn_\eta}\rangle d^{(\pm)}_{nn_\eta}\Big]$$

$$E_n=-Z^2/2n^2$$

ELECTRONIC ENERGIES FOR $1s\sigma$ STATE

	$\varepsilon_{1s\sigma}^{(+)}(R)\,au$			
$R\,au$	$Z=1$	$Z\neq 1$	$Z\neq 1$	[illegible] values
0.25	-1.4754	-1.8980	-1.8981	-1.8986
0.5	-1.4213	-1.7318	-1.7319	-1.7350
0.75	-1.3560	-1.5753	-1.5757	-1.5824
1.0	-1.2884	-1.4410	-1.4418	-1.4518
1.25	-1.2230	-1.3283	-1.3295	-1.3418
1.50	-1.1617	-1.2338	-1.2353	-1.2490
1.75	-1.1053	-1.1541	-1.1559	-1.1701
2.0	-1.0538	-1.0865	-1.0885	-1.1026
2.25	-1.0071	-1.0286	-1.0307	-1.0444
2.5	-0.9648	-0.9788	-0.9808	-0.9938
2.75	-0.9267	-0.9355	-0.9376	-0.9497
3.0	-0.8924	-0.8978	-0.8998	-0.9109
3.5	-0.8339	-0.8357	-0.8375	-0.8466
4.0	-0.7869	-0.7873	-0.7898	-0.7961
4.5	-0.7493	-0.7493	-0.7506	-0.7562
5.0	-0.7192	-0.7192	-0.7202	-0.7244
6.0	-0.6757	-0.6757	-0.6763	-0.6786
7.0	-0.6469	-0.6469	-0.6472	-0.6485
8.0	-0.6267	-0.6267	-0.6269	-0.6276
9.0	-0.6118	-0.6118	-0.6119	-0.6123
10.0	-0.6003	-0.6003	-0.6004	-0.6006
12.0	-0.5834	-0.5834	-0.5834	-0.5835
16.0	-0.5625	-0.5625	-0.5625	-0.5625
20.0	-0.5500	-0.5500	-0.5500	-0.5500

ELECTRONIC ENERGIES FOR $2p\pi$ STATE

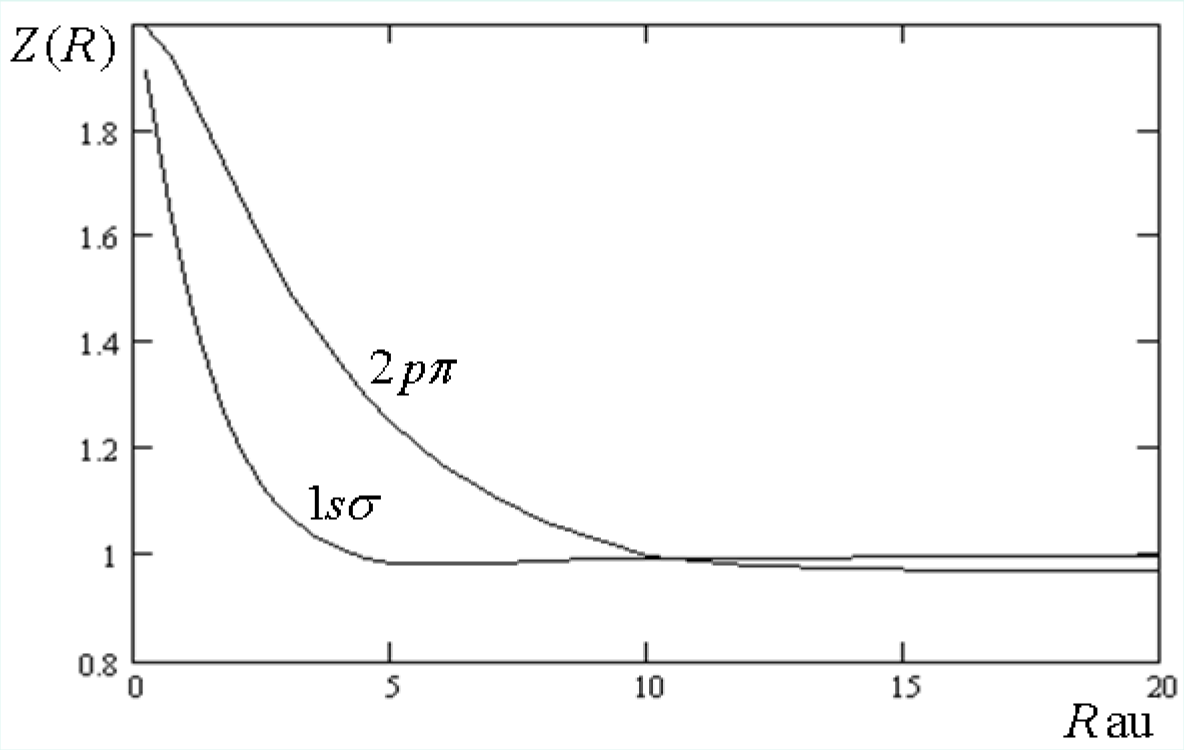
	$\varepsilon_{2p\pi}^{(+)}(R)\,au$			
$R\,au$	$Z=1$	$Z\neq 1$	$Z\neq 1$	values
0.25	-0.3746	-0.4880	-0.4980	-0.4980
0.5	-0.3735	-0.4923	-0.4923	-0.4923
0.75	-0.3716	-0.4839	-0.4839	-0.4841
1.0	-0.3692	-0.4736	-0.4737	-0.4741
1.25	-0.3662	-0.4622	-0.4623	-0.4631
1.50	-0.3627	-0.4503	-0.4504	-0.4517
1.75	-0.3589	-0.4380	-0.4382	-0.4402
2.0	-0.3548	-0.4259	-0.4261	-0.4288
2.25	-0.3504	-0.4140	-0.4143	-0.4176
2.5	-0.3458	-0.4025	-0.4029	-0.4068
2.75	-0.3411	-0.3914	-0.3919	-0.3964
3.0	-0.3363	-0.3808	-0.3814	-0.3864
3.5	-0.3266	-0.3610	-0.3619	-0.3678
4.0	-0.3169	-0.3432	-0.3443	-0.3508
4.5	-0.3073	-0.3272	-0.3285	-0.3354
5.0	-0.2979	-0.3129	-0.3143	-0.3214
6.0	-0.2803	-0.2884	-0.2899	-0.2970
7.0	-0.2642	-0.2684	-0.2699	-0.2766
8.0	-0.2499	-0.2519	-0.2534	-0.2595
9.0	-0.2374	-0.2383	-0.2397	-0.2450
10.0	-0.2265	-0.2269	-0.2282	-0.2327
12.0	-0.2092	-0.2092	-0.2102	-0.2133
16.0	-0.1871	-0.1871	-0.1876	-0.1888
20.0	-0.1745	-0.1745	-0.1747	-0.1751

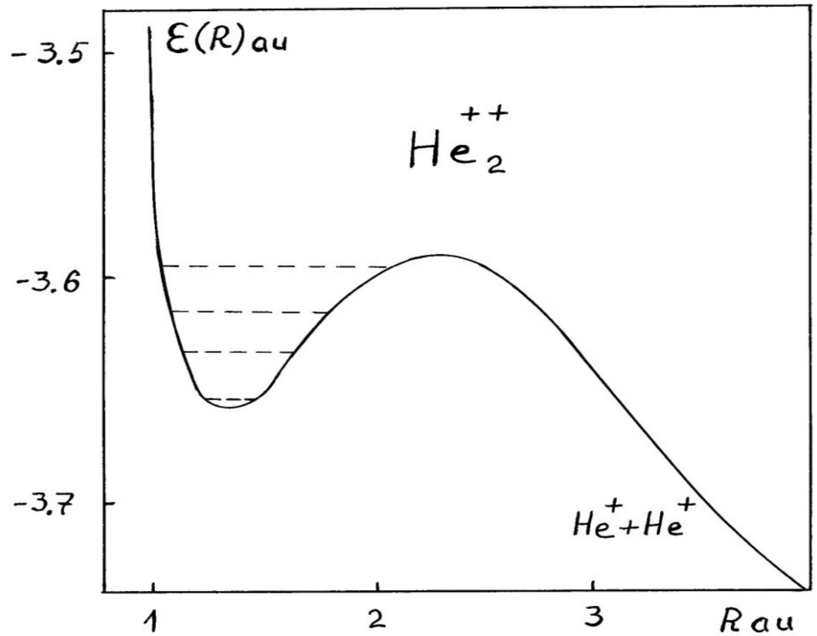
VARIATIONAL PRINCIPLE

$$\varepsilon_i^{(\pm)}(Z,R) = \frac{\langle \Phi_i^{(\pm)}(\xi,\eta,R) \left| \hat{H} \right| \Phi_i^{(\pm)}(\xi,\eta,R) \rangle}{\langle \Phi_i^{(\pm)}(\xi,\eta,R) \left| \Phi_i^{(\pm)}(\xi,\eta,R) \right\rangle}$$

$$\frac{d\varepsilon_i^{(\pm)}(Z,R)}{dZ} = 0$$

THE EFFECTIVE CHARGE AS A FUNCTION OF R





$R_o = 1.35$ au $\quad R_{max} = 2.2$ au

$\tau_o = 10^{16}$ sec $\quad \tau_4 = 10^{-12}$ sec

$D = 1.69$ eV $\quad D_{bottom} = 6.34$ eV

MOLECULAR ORBITAL CORRELATION RULE

$$n_r \equiv n_u - l_u - 1 = n_\xi$$

$$l_u - m = 2n_\eta \qquad l_u - m = 2n_\eta + 1$$

$$n_u = n + n_\eta$$
$$l_u = 2n_\eta + m$$

[illegible]

$$n_u = n + n_\eta + 1$$
$$l_u = 2n_\eta + m + 1$$

[illegible]

Thank you for attention!