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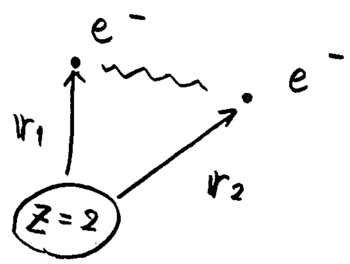
4. 原子, 分子の構造

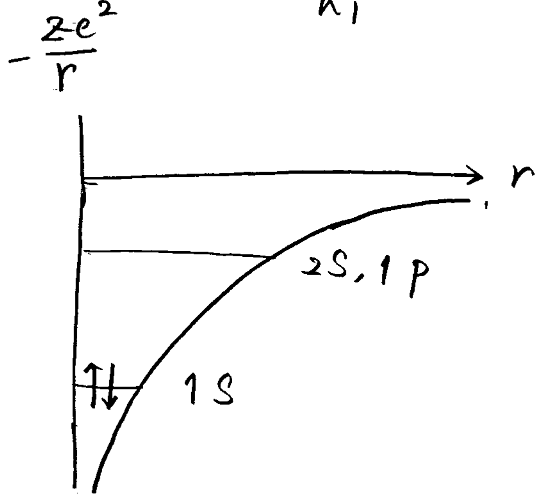
4.1. He 原子の構造



$$H = \frac{\mathbb{P}_1^2}{2m} + \frac{\mathbb{P}_2^2}{2m} - \frac{Ze^2}{r_1} - \frac{Ze^2}{r_2} + \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

◦ 電子間相互作用を無視する近似

$$H_0 = \underbrace{\frac{\mathbb{P}_1^2}{2m} - \frac{Ze^2}{r_1}}_{h_1} + \underbrace{\frac{\mathbb{P}_2^2}{2m} - \frac{Ze^2}{r_2}}_{h_2}$$



$$\psi_{1s}(\mathbf{r}) = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0} \times \frac{1}{\sqrt{4\pi}}$$

$$a_0 = \hbar / mc\alpha$$

$$\Psi_{gs}^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\,\psi_{1s}(\mathbf{r}_2) \cdot \underbrace{\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)}_{|S=0\rangle}$$

↑
反対称化スピン波動関数

$$E_{gs}^{(0)} = 2E_{1s} = -mc^2(2\alpha)^2 = -108.8\,eV$$

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(note) ハミルトニアンを正確に解くと (数値計算)

$$E_{gs} = -78.975 \text{ eV}$$

◦ 電子間相互作用の効果

摂動論で見積もると,

$$\Delta E = \langle \Psi_{gs}^{(0)} | V_{ee} | \Psi_{gs}^{(0)} \rangle$$

$$= \int d\mathbf{r}_1 d\mathbf{r}_2 \, \Psi_{gs}^{(0)}(\mathbf{r}_1, \mathbf{r}_2)^* V_{ee}(\mathbf{r}_1, \mathbf{r}_2) \Psi_{gs}^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$$

$$= \int d\mathbf{r}_1 d\mathbf{r}_2 \, |\psi_{1s}(\mathbf{r}_1)|^2 |\psi_{1s}(\mathbf{r}_2)|^2 \cdot \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

$$= \cdots = \frac{5}{8} \frac{Ze^2}{a_0}$$

↓

$$E_{gs}^{(1)} = E_{gs}^{(0)} + \Delta E = -108.8 + 34 \text{ eV}$$

$$= -74.8 \text{ eV}$$

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○ よりよい近似

$$\Psi_{gs}(\mathbf{r}_1, \mathbf{r}_2) \sim \tilde{\psi}_{1s}(\mathbf{r}_1)\, \tilde{\psi}_{1s}(\mathbf{r}_2)\ |S=0\rangle$$

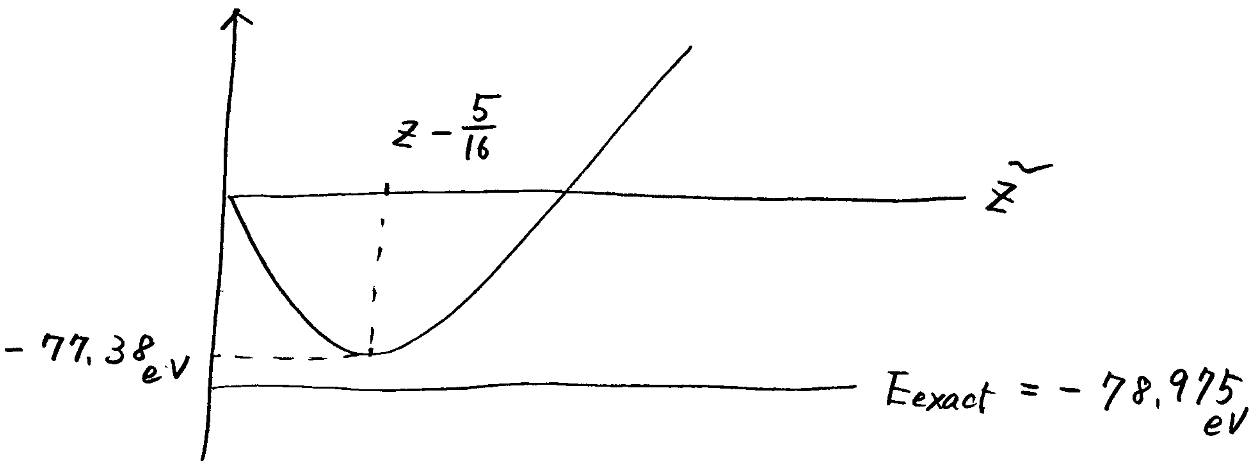
$$\tilde{\psi}_{1s}(\mathbf{r}) = 2\left(\frac{\tilde{Z}}{a_0}\right)^{\frac{3}{2}} e^{-\tilde{Z}r/a_0} \cdot \frac{1}{\sqrt{4\pi}}$$

別の電子がいることにより原子核の電荷が
「遮へい」されるかもしれない

$\downarrow \quad Z \to \tilde{Z} \qquad \left[-\frac{Ze^2}{r} \to -\frac{\tilde{Z}e^2}{r} \right]$

$\tilde{Z}$ は変分法で求める

$$E(\tilde{Z}) = \langle \Psi_{gs} | H | \Psi_{gs} \rangle$$



○ さらによい近似
r ごとに $\tilde{Z}$ の値を変える（ハートリー・フォック近似）

$$-\frac{Ze^2}{r} \to -\frac{\tilde{Z}(r)e^2}{r}$$

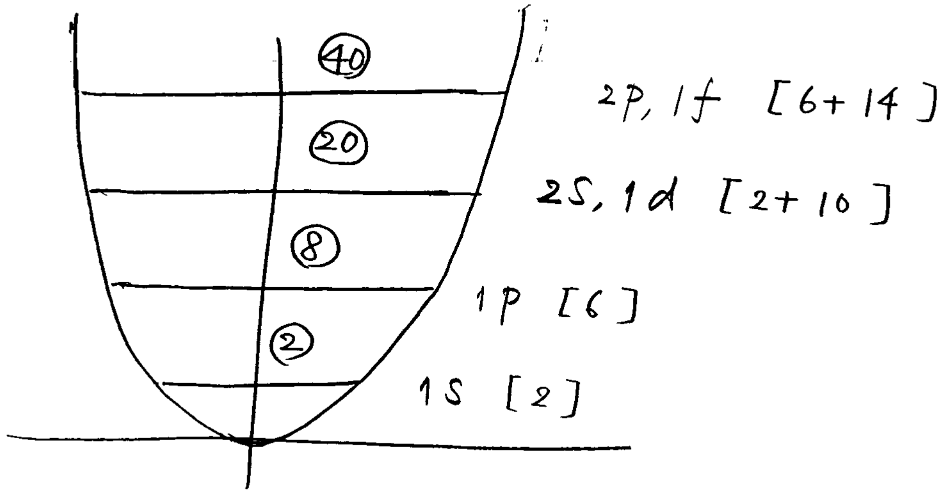
$$\downarrow \quad E_{gs}^{(HF)} = -77.87\ \mathrm{eV}$$

(余談) 原子核の構造

魔法の数： 2, 8, 20, 28, 50, 82, 126

調和振動子ポテンシャルに核子をつめる

$$V(r) = \frac{1}{2} m\omega^2 r^2$$



$$E_{n\ell} = \left(2(n-1) + \ell + \frac{3}{2}\right)\hbar\omega$$

スピン

縮退度： $2 \times (2\ell + 1)$

※ スピン・軌道力が大きな役割

$$V(r) = \frac{1}{2} m\omega^2 r^2 + \alpha\, \vec{\ell} \cdot \vec{s}$$

(note) $j = \ell + s$ $\downarrow$ $\ell \cdot s = \frac{1}{2}(j^2 - \ell^2 - s^2)$

$$j = \ell \pm \frac{1}{2}$$

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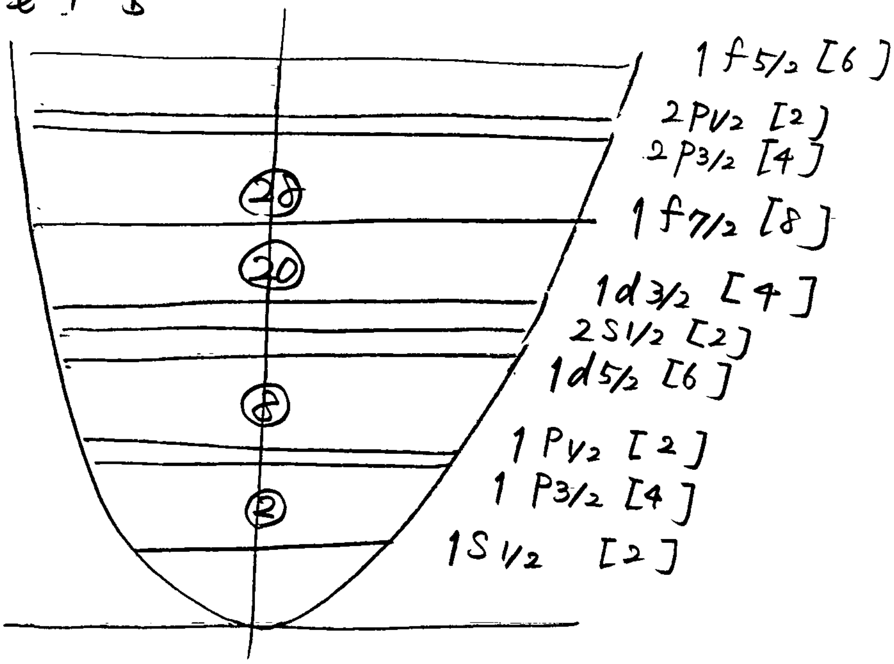
$j = l + s$



$1f \longrightarrow 1f_{7/2}$ と $1f_{5/2}$ に分離

$(14 = 8 + 6)$

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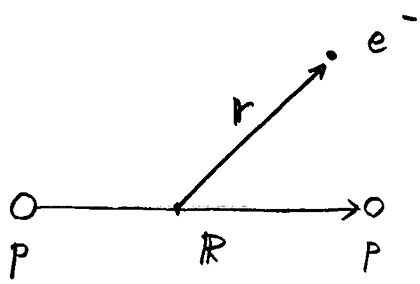
4.2. 分子の構造

○ 断熱近似（ボルン・オッペンハイマー近似）

最も単純な分子： H_2^+



$$H = -\frac{\hbar^2}{2\mu}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_r^2 + \frac{e^2}{R} - \frac{e^2}{|\mathbf{r}+\frac{\mathbf{R}}{2}|} - \frac{e^2}{|\mathbf{r}-\frac{\mathbf{R}}{2}|}$$

$$\mu = \frac{m_p}{2} \sim \frac{940}{2}\ (\mathrm{MeV}/c^2) = 470\ (\mathrm{MeV}/c^2)$$

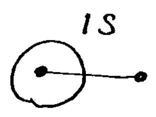
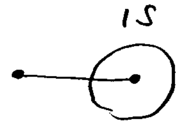
$$m \sim m_e = 0{,}5\ (\mathrm{MeV}/c^2)$$

$\mu \gg m_e$ → 陽子は相対距離 R で固定
（止まっている）

↓

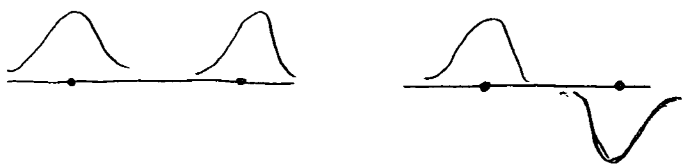
$$\underbrace{\left(-\frac{\hbar^2}{2m}\nabla_r^2 - \frac{e^2}{|\mathbf{r}+\frac{\mathbf{R}}{2}|} - \frac{e^2}{|\mathbf{r}-\frac{\mathbf{R}}{2}|}\right)}_{\equiv\ h_e} \varphi_{\mathbf{R}}(\mathbf{r}) = \varepsilon(\mathbf{R})\,\varphi_{\mathbf{R}}(\mathbf{r})$$

∘ 線形結合近似

$|\varphi_{\mathbb{R}}^{(\pm)}\rangle \sim |$  $\rangle \pm |$  $\rangle$

$$= C_\pm(R)\Big(\underbrace{\psi_{1s}(\mathbf{r}-\tfrac{\mathbb{R}}{2})}_{\substack{\parallel\\ \psi_{1s}(L)}} \pm \underbrace{\psi_{1s}(\mathbf{r}+\tfrac{\mathbb{R}}{2})}_{\substack{\parallel\\ \psi_{1s}(R)}}\Big)$$

規格化：



$$1 = \langle \varphi_{\mathbb{R}}^{(\pm)} | \varphi_{\mathbb{R}}^{(\pm)} \rangle$$

$$= |C_\pm(R)|^2 \langle \psi_{1s}(L) \pm \psi_{1s}(R) | \psi_{1s}(L) \pm \psi_{1s}(R) \rangle$$

$$= |C_\pm(R)|^2 \Big\{ \langle \psi_{1s}(L)|\psi_{1s}(L)\rangle + \langle \psi_{1s}(R)|\psi_{1s}(R)\rangle \pm \langle \psi_{1s}(L)|\psi_{1s}(R)\rangle + \langle \psi_{1s}(R)|\psi_{1s}(L)\rangle \Big\}$$

$$= |C_\pm(R)|^2 \Big\{ 2 \pm 2 \underbrace{\int d\mathbf{r}\, \psi_{1s}(\mathbf{r}-\tfrac{\mathbb{R}}{2})^* \psi_{1s}(\mathbf{r}+\tfrac{\mathbb{R}}{2})}_{\equiv S(R)} \Big\}$$

$$\equiv S(R) = \cdots = \left(1 + \frac{R}{a_0} + \frac{R^2}{3a_0^2}\right) e^{-R/a_0}$$

$$\hookrightarrow \begin{cases} \to 0 & (R\to 0) \\ \to 1 & (R\to 0) \end{cases}$$

$\downarrow$

$$|C_\pm(R)|^2 = \frac{1}{2(1\pm S(R))}$$

エネルギー

$$\mathcal{E}_\pm(R) = |C_\pm(R)|^2 \langle \psi_{1s}(L) \pm \psi_{1s}(R) | h_e | \psi_{1s}(L) \pm \psi_{1s}(R) \rangle$$

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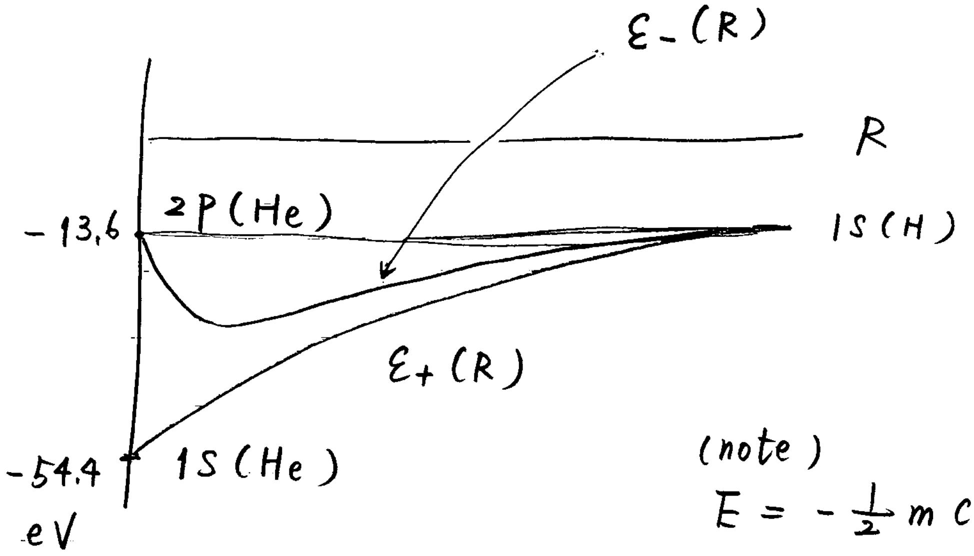

(note)

$$E = -\frac{1}{2} m c^2 \cdot \frac{(Ze)^2}{n^2}$$

(note) $|\varphi_R^{(+)}\rangle \longrightarrow |\psi_{1s}(He)\rangle$

$$|\varphi_R^{(-)}\rangle \xrightarrow[R\to 0]{} |\psi_{2p}(He)\rangle$$

2つの陽子の入れかえに対し反対称
(パリティ：マイナス)

○基底状態