Qüestions T4

1. $[1s^2\ 2s^2]\ 2p^4\ 3s^1$

$p^4 : {}^3P,\ {}^1D,\ {}^1S$

$s^1 : {}^2S$

$(l=0\ \ s=1/2)$

$L_T = l+l,\ l-l \ldots$

$S_T = s+s,\ s-s \ldots$

$\boxed{{}^3P,\ {}^2S}$ $\quad L_T = 0+1 = 1$

$S_T = 1+1/2,\ 1+1/2-1,\ 1-1/2 = 3/2,\ 1/2.$ $\quad {}^4P,\ {}^2P$

$\boxed{{}^1D,\ {}^2S}$ $\quad L_T = 2$

$S_T = 0+1/2 = 1/2$ $\quad {}^2D$

${}^1S,\ {}^2S$ $\quad L_T = 0 \quad S_T = 1/2$ $\quad {}^2S$

E) ${}^4P,\ {}^2P,\ {}^2D,\ {}^2S$ ✓

2. |Slater| certa: nº variables ≠ nº OAs ~~[illegible]~~ α = nº ~~[illegible]~~ = $\boxed{n^{e^-} \times 4}$ ok

Coord. r i ~~x~~ noves r

E) Nº variables = nº e^- ×4 ✓

3. Aprox. BO: sep ~~rot vib~~ $\hat{H}$ ~~sep~~ Implica dependència mov. nuc – estat e^-.

nuclis fixos en Re (0,0)

D) Implica dep. mov. nuc – estat e^-. ✓

4. Mètode CI: permet apropar-se més que HF a E exacta.

F. $\Sigma c_i \Phi_s$ c_i ~~prefixats~~ els volem optimitzar

A) Apropar-se més que HF a E^{ex}! ✓

5. HF no hi poden haver +2e⁻ = orbital

C) I^{HF} s'anul·laria (Pauli) ✓

6. Quina config correspon + det Slater?

A) $2p^1\ 3d^1$ ⑥ $+ \binom{10}{1} = 10 \rightarrow$ ~~16~~ $\rightarrow 60$

B) $2p^2\ 3p^1$ $\binom{6}{2} = \frac{6\cdot5}{2\cdot1} = 15 + \binom{6}{1} = 6+15 =$ ~~21~~

C) $2p^3\ 3s^1 \rightarrow \binom{6}{3} = \frac{6\cdot5\cdot4}{3\cdot2\cdot1} = 20 \times \binom{2}{1} =$ ~~22~~ 40

D) $2p^4\ 3s^1$ $\binom{6}{4} = \frac{6\cdot5}{2\cdot1} = 15 \times \binom{2}{1} =$ ~~17~~ 30

~~C)~~ $2p^3\ 3s^1$

B) $2p^2\ 3p^1$ ✓ $\quad 6 \times 15 = 90$

7. Valor en U.A tendeix E_{el} sense V_{n-n} de iò HeH^{2+} quan $R \rightarrow 0$

$E(Na) = -\frac{3^2}{2\cdot n^2} = -\frac{9}{2}$ $\quad$ E) $-9/2$ ✓

8. HF Roothaan funcions de base:

A) linealment independents. ✓

9. |Slater| ~~simètrica~~ antisimètrica (e^-) ~~simètrica nuclis)~~

~~D)~~ B) Anti e^- No depèn nuclis.

10. |Slater| $3s^1\ 4p^2\ 4d^1$: $\binom{2}{1} = 2 \times \binom{6}{2} = \frac{6\cdot5}{2} = 15 \times \binom{10}{1} = 10$

B) 300 (2×15×10) ✓

11. $\hat{H}_{el}$ de H-F : $\hat{T}_{el} + \hat{V}_{el} + \hat{V}_{n-e}$ té $10e^-$ $Z(F) = 9$

✓ C) $\hat{H}_{el} = -\sum_{i=1}^{10} \frac{1}{2}\nabla_i^2 + \sum^{9}\sum^{10} \frac{1}{r_{ij}} - \sum^{10} 1/r_{iH} - \sum^{10} \frac{9}{r_{iF}}$

12. $j_1 = 1, j_2 = 2, j_3 = 1$

1+2 → $J_T = 3, 2, 1$ | 2+1 → $J_T = 3, 2, 1$ | D) 4, 3, 3, 2, 2, 2, 1, 1, 1, 0 ✓

3+1 → $J_T = 4, 3, 2, 1$ | 1+1 → $J_T = 2, 1, 0$

13. HF funció de prova variacional.
D) Un det. de Slater ✓

14. Config e⁻ : $|\Phi_{1s}\alpha\,\Phi_{1s}\beta\,\Phi_{2s}\alpha\,\Phi_{2s}\beta\,\Phi_{2px}\alpha|$
D) $1s^2 2s^2 2p^1$ ✓

15. HF : $\hat{f}\Psi = E_i \Psi_i$ sistema pol·e⁻ → iterem: perquè?
A) Perquè f depèn Φ pròpies!! $f = \hat{h} + V_{rep}(\{\Phi\})$ ✓

16. He si no hi ha rep entre e⁻ Φ_{1s} 1s → Z = 2.
C) $\Psi = \Phi_{1s}(1)\,\alpha(\omega_1)\,\Phi_{1s}(2)\,\beta(\omega_2) - \Phi_{1s}(2)\,\alpha(\omega_2)\,\Phi_{1s}(r_1)\,\beta(\omega_1)$ ✓

17. Càlcul HF Roothaan H_2O base mínima $E_{el} = -83{,}87$ hartree $V_{rep\,n-n} = 8{,}906524$ hartree
Si ho fem H_2O^+ → ≠ Eel = Vrep n-n C) ✓

18. HF falsa: Teorema variacional ✓ |Slater| ✓ Càlcul f. pròpies $\hat{f}$ (depèn f. pròpies) ✓
A) É anomenada electrons en estat fonamental ~~nuclis~~ ✓✓

19. Eel diatòmica R → ? quan R → 0 ,
D) Eel àtom $Z = \sum Z_i$ ✓

20. $3d^9 4s^1 4p^1$: Cu :

$d^9 = d^1$ → L = 2, S = 1/2 → ^2D

s^1 → L = 0, S = 1/2 → ^2S

} $L_T = 2$, $S_T = 1, 0$ → ^3D ^1D

p^1 → L = 1, S = 1/2 → ^2P

} $L_T = 3, 2, 1$, $S_T = 3/2, 1/2$ → ^4F ^4D ^4P / ^2F ^2D ^2P

^1D, ^2P → $L_T = 3, 2, 1$, $S_T = 1/2$ } ^2F ^2D ^2P

E) $^4F\,^4D\,^4P$, $^2F\,^2D\,^2P$, $^2F\,^2D\,^2P$. ✓

22. $\hat{H}_{el}$ inclou termes $\hat{H}$ que depenen de coord. e⁻
A) ✓

23. HF de C_{60} : A) depèn geometria que s'empri per fer el càlcul. ✓

~~24~~. 25. Ψ ($^2H_2$) completa S = 1 simètrica respecte nuclis
D) ✓ antisimètrica respecte e⁻

26. nº |Slater| $2s^1 2p^2$ ~~$3s^2$~~ (7e⁻) 2 × 15 = 30
D) 30 ✓

27. C) Hèlode CI és variacional.
BO: nuclis sí que depèn e^-. $E_T \neq E_{el} + E_{nuc}$ (F)
Pot electrònic nº parell e^- → capa tancada p^6 d^{10} f^{14}!

28. C) Falsa: Hexcanviar r i w de 2 part idèntiques $s = 1/2$ ψ canvia de signe!!!

29. 2 partícules ≠ $J_1^2 = 2$; $J_2^2 = 12$ → J_T^2 ?

$j_1 = 1$, $j_2 = 3$ { $J_T = 4, 3, 2$ → $J_T^2 = 4(4+1) = 20$; $3(3+1) = 12$; $2(2+1) = 6$

c) 20, 12, 6

30. [Al] 13 e^- $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$ → $s = 1/2$, $L = 1$ } ^2P

$\binom{6}{1} = 6$ B) 2P, 6 det Slater

31. HF molècula falsa?
B) HF no descriu correctament la rep. internuclear! ??

33. Schrödinger e^- falsa: NO representa E_T sinó E_{el}
b) ~~E~~

34. Variables Slater HF? $4 \times 4 = 16$ e^- D)

35. Àtom i mol. amb = nº e^-
SO → Slater OK (A) Hel és (E) NO!! Vnuc molècula té + nuclis

36. HF: \Slater\ no és pròpia d'$\hat{A}$ (f).
B) \Slater\ HF millor funció de variacional

37. $\hat{H}_{el}$ (H) $= -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} + \frac{1}{r_{12}}$
D)

38. $3d^1\ 4s^1\ 4p^1$ $10 \times 2 \times 6 = 120$ \Slater\ valors ≠ E?

d^1 → $L = 2$, $s = 1/2$ } $L_T = 2$, $S_T = 1, 0$ } ^3D ^1D

s^1 → $L = 0$, $s = 1/2$

p^1 → $L = 1$, $s = 1/2$ } ^3D ^2P } $L_T = 3, 2, 1$, $S_T = 3/2, 1/2$ } ^4F ^4D ^4P ^2F ^2D ^2P

^1D ^2P } $L_T = 3, 2, 1$, $S_T = 1/2$ } ^2F ^2D ^2P

B) 120 \Slater\ i 9 E

39. $|\Phi_{1s}\,\alpha(1)\,\Phi_{2s}\,\beta(2)|$
$L_z = 0$ $L_z = 0$ → $L_T = 0$
$S_z = 1/2$ $S = 1/2$ $L_S = X, 0$

A) $M_L = 0$ i $M_S = 0$

40. $d = 0,5292$ Å $E_{el} = -469,96869$ Ha. $Z(A) = 17$ $Z(B) = 1$ U?

$V_{n\text{-}n} = \sum\sum \frac{1}{4\pi\varepsilon_0} \cdot \frac{17 \cdot 1\, e^2}{r_{AB}} = \frac{17}{0,5292}$ ~~= 32,12 Ha~~ = 17 hartree

1 Å = 10^{-10} m $a_0 = 0,5292$ Å = 1 UA

$U = -469 + 17 = -452,97$ Ha C)

41. He: $1s^1 2s^1 \rightarrow {}^1S$; ${}^3S$ C) ✓
s^2 S_T = ~~2~~ → ~~^3S~~ $S_T = 0$ s'anul·la ✓ (${}^1S$) Capa plena
$L_T = 0$

42. Termes espectrals depenen e^- → B) ✓ $\hat{H} = T_e + V_{ne} + V_{ee}$

~~43.~~ 44. | Slater | D) canvi columnes canvi signe! ✓

45. = geometria C) ✓ V_{nucli} (=) $E_{el} \neq$ pq no estan degenerats!!

46. Termes no inclòs $\hat{H}_{el}$ $\hat{T}_n$ D) ✓

47. C) ✓

49. HF no fa servir O virtuals | Slater | C) ✓

50. E_{el} CLOA // HF Roothan.
A) OMs → Σc_i OAs! ✓

~~51.~~ 52. | Slater | C) 1 sol det / confis NO!! ✓

53. C) ✓ Bescanvi r i ω canvi signe.

54. RHF → H1 (A) ✓ ~~EHF~~ + V_{n-n} → U

55. E(TE) > E(confis) A) ✓

56. $\binom{6}{2} = 15$ $\binom{6}{3} = \frac{654}{321} = 20$ → 300 A) ✓

57. a) $p^5 = (p^1)$
b) p^3: ^4S, ^2D ^2P
~~c) ^1S~~
B) p^3 ✓
d) $s^1 3d^1$
L=0 S=1/2 L=2 s=1/2 $L_T = 2$, $S_T = 1, 0$ { ^1D ^3D

~~58.~~ 59. $\binom{6}{5} = \frac{65432}{54321} = 6 \times 2 = 12$ C) ✓

60. $\hat{f}$ operador monoelectrònic D) ✓

61. RHF: C) 1 | Slater | funció prova. ✓

62. H_2 i H_2^+ = V_{nn} ≠ E_{el} A) ✓

63. H_2O CI → 24 | Slater | coord. e^-? C) ✓
2+8e⁻ → 10e⁻ ×4 = 40 ✓

~~64.~~
65. D) ✓

66. S.Orb. no anti 2e⁻ pq s'anul·la. D) ✓

67. L=0, S_T=1 | J= | L=0, S=0 { (${}^1S$) D) interacció s.orb =0
L=2, S=0 | (L=1, S=1) ~~D)~~ C

68. B) ✓

69. –

70. Variables (OM) nº e^- = 16 OM (x, y, z) → 3 (D) ✓

71. -E ↑S ↑L → ~~3d¹ ... = 1·(4+1)~~ =
Calcular termes espectrals! –

72. RHF Roothan E^{HF} ≠ Σ ε OMs ocupats!! B) ✓

73. variables d' espai Φ_{slater} i |Slater| si n = 10:
r = 3 3 × 10 = 30

B) 3 i 30 ✓

74. V_{nn} (HCN) = $\sum\sum \frac{Z_A Z_B}{R_{AB}}$ = $\frac{1\cdot6}{2} + \frac{6\cdot7}{3} + \frac{1\cdot7}{5}$ = 18,4 D) ✓

H — C — N
2bohrs 3bohrs

~~75.~~ 76. Falsa. singulet (S=0) no presenta interacció ✓
s (l=0) " " ✓
Enivells ↓ respecte els de partida NO!! (C) ✓
A vegades int. SO no trenca degeneració, es desdoblen si hi ha més d'1 nivell!!
↳ pq no hi ha. Quan S=0 i/o L=0

~~77.~~ 78. Molècula ne^- E^{HF} = ∫ variacional |Slater|^{HF} (A) ✓

79. |Slater| elements: Φ variables r i ω d'un e^- D) ✓

80. C) $|\Psi(1,2)|^2 = |\Psi(2,1)|^2$ ✓

81. n spin orbitals ≠. ⇒ |Slater| B) ✓

82. B) ✓ 84. A) OMs = Σ c_i OAs ✓

83. C) ✓ ~~85~~ ~~86~~ ~~87~~

88. H_2S H–S–H 90° d = 1,0584 = (2) u.a 2, 2 h = $\sqrt{4+4} = \sqrt{8}$

$V = \frac{1\cdot1}{\sqrt{8}} + \frac{1\cdot16}{2} + \frac{1\cdot16}{2}$ = 16,35 (A) ✓

89. HF O. virtuals |Slater| NO! B) ✓

~~90.~~ 91 C_2H_4 (C) ✓

92. $\hat{S}^2 = S(S+1)\hbar^2 = \frac{1}{2}\frac{3}{2}\hbar^2 = 3/4\hbar^2$ sempre raonar (C) ✓
S = 1/2

93. (B) ✓ 94. 3, 4, 4×6 = 24 (C) ✓

95. (A) ✓

96. $r_1 \leftrightarrow r_2$ $\omega_1 \leftrightarrow \omega_2$ partícules distingibles $|\Psi|^2 = -|\Psi|^2$!! (A) ✓

97. $j_1^2 = 2$, $j_2^2 = 6$ } J_T^2 ?

$j_1 = 1$, $j_2 = 2$ } $J_T = 3, 2, 1$

$J_T^2 = 3(4) = 12$
$= 2(3) = 6$
$= 1(2) = 2$

D) 12, 6, 2 ✓

~~98~~ 99. (A) ~~perturbacions~~ ✓ , Mirar !!

~~100.~~

101. ~~(A)~~ C

102. $3 \times 4 = 12$ $3 \times 3 = 9$ (A) ✓

103. (B) ✓ 105. C) ✓

104. (C) ✓ 106. SCF: procediment iteratiu. (B) ✓

107. ~~(C)~~ A

108. $\hat{L}^2 = 0$, $\hat{S}^2 = \cancel{3}/4$ ~~(C)~~ A

(ca: 0, pq tots e... 1S)

H–O–H (angle) $h = \sqrt{2}$

Eel = −83,80 V ?

$$V = \frac{8 \cdot 1}{1} + \frac{8 \cdot 1}{1} + \frac{1 \cdot 1}{\sqrt{2}} = 16 + \frac{1}{\sqrt{2}} = 16{,}707 \text{ Å}^{-1} \cdot \frac{10^{10} \text{ Å}}{1 \text{ m}} \cdot \frac{5{,}292 \cdot 10^{-11} \text{ m}}{1 \text{ u.a.}}$$

(A) ~~V = 67,055~~