

Supporting Information

Solvent and pH effects on the ionization energies of bioorganic molecules: A case study of Alanine and Glycine

Ravi Kumar^{*a}, Aryya Ghosh,^{b‡} and Nayana Vaval^{*a}

February 18, 2026

Contents

| | |
|--|-----------|
| 1 Mulliken Spin Populations for all Glycine forms | 2 |
| 1.1 Neutral Glycine - Gas and PCM | 2 |
| 1.2 Glycine Zwitterion - Gas and PCM | 2 |
| 1.3 Deprotonated Glycine - Gas and PCM | 2 |
| 1.4 Protonated Glycine - Gas and PCM | 2 |
| 2 Alanine Mulliken Spin Populations | 3 |
| 2.1 Alanine Neutral - Gas and PCM | 3 |
| 2.2 Alanine Zwitterion - Gas and PCM | 3 |
| 2.3 Deprotonated Alanine - Gas and PCM | 3 |
| 2.4 Protonated Alanine - Gas and PCM | 3 |
| 3 All CAS involved Molecular Orbitals (MO) for Neutral Glycine | 4 |
| 4 All CAS involved Molecular Orbitals (MO) for Zwitterion Glycine | 5 |
| 5 All CAS involved Molecular Orbitals (MO) for Deprotonated Glycine | 6 |
| 6 All CAS involved Molecular Orbitals (MO) for Protonated Glycine | 7 |
| 7 All CAS involved Molecular Orbitals (MOs) for Neutral Alanine | 9 |
| 8 All CAS-involved molecular orbitals (MOs) for zwitterionic alanine. | 10 |
| 9 All CAS involved Molecular Orbitals (MOs) for Deprotonated Alanine | 11 |
| 10 All CAS involved Molecular Orbitals (MOs) for Protonated Alanine | 13 |

^{0a}Physical and Materials Chemistry Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, 411008, India.

^{0a}Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India Tel: +91 2590 2499; E-mail:np.vaval@ncl.res.in

^{0b}Department of Chemistry, Ashoka University, Sonapat, Haryana,131029 India

1 Mulliken Spin Populations for all Glycine forms

Note: O1 is the oxygen atom of the carbonyl group (C=O) within the -COOH moiety and the O2 is the oxygen atom of hydroxyl group (-OH) within the same moiety. This notation is applicable to all form of glycine.

1.1 Neutral Glycine - Gas and PCM

| Phase | Basis (2s) | N | C1 | C2 | O1 | O2 | Dominating AO |
|-------|------------|--------|--------|--------|--------|--------|---------------|
| Gas | Root 12 | 0.1069 | 0.3634 | 0.1343 | 0.0184 | 0.0090 | C1-2s |
| Gas | Root 13 | 0.6747 | 0.2544 | 0.0058 | 0.0107 | 0.0005 | N-2s |
| Gas | Root 14 | 0.0025 | 0.0028 | 0.0594 | 0.5534 | 0.2600 | O1-2s |
| Gas | Root 15 | 0.0009 | 0.0122 | 0.2917 | 0.1934 | 0.5660 | O2-2s |
| PCM | Root 12 | 0.0968 | 0.3243 | 0.1702 | 0.0217 | 0.0089 | C1-2s |
| PCM | Root 13 | 0.6857 | 0.2473 | 0.0083 | 0.0077 | 0.0005 | N-2s |
| PCM | Root 14 | 0.0014 | 0.0017 | 0.0523 | 0.5481 | 0.2737 | O1-2s |
| PCM | Root 15 | 0.0006 | 0.0100 | 0.2879 | 0.2091 | 0.5548 | O2-2s |

1.2 Glycine Zwitterion - Gas and PCM

| Phase | Basis (2s) | N | C1 | C2 | O1 | O2 | Dominating AO |
|-------|------------|--------|--------|--------|--------|--------|---------------|
| Gas | Root 12 | 0.0233 | 0.5935 | 0.0262 | 0.0142 | 0.0199 | C1-2s |
| Gas | Root 13 | 0.0078 | 0.0030 | 0.0006 | 0.4059 | 0.4047 | O1-2s |
| Gas | Root 14 | 0.2689 | 0.0042 | 0.2515 | 0.2128 | 0.2780 | O2-2s |
| Gas | Root 15 | 0.5337 | 0.1211 | 0.1617 | 0.1466 | 0.0738 | N-2s |
| PCM | Root 12 | 0.0305 | 0.5851 | 0.0394 | 0.0147 | 0.0185 | C1-2s |
| PCM | Root 13 | 0.0490 | 0.0066 | 0.0036 | 0.4825 | 0.2904 | O1-2s |
| PCM | Root 14 | 0.6798 | 0.0742 | 0.0193 | 0.0002 | 0.1326 | N-2s |
| PCM | Root 15 | 0.0767 | 0.0537 | 0.3835 | 0.2836 | 0.3458 | O2-2s |

1.3 Deprotonated Glycine - Gas and PCM

| Phase | Basis | N | C1 | C2 | O1 | O2 | Dominating AO |
|-------|---------|--------|--------|---------|--------|--------|---------------|
| Gas | Root 12 | 0.0742 | 0.5000 | 0.0447 | 0.0101 | 0.0224 | C1-2s |
| Gas | Root 13 | 0.6645 | 0.1829 | -0.0006 | 0.0646 | 0.0035 | N-2s |
| Gas | Root 14 | 0.0420 | 0.0069 | 0.0001 | 0.3577 | 0.4241 | O2-2s |
| Gas | Root 15 | 0.0092 | 0.0323 | 0.4005 | 0.3535 | 0.3419 | O1-2s |
| PCM | Root 12 | 0.0865 | 0.4709 | 0.0699 | 0.0119 | 0.0230 | C1-2s |
| PCM | Root 13 | 0.6985 | 0.2122 | 0.0007 | 0.0148 | 0.0008 | N-2s |
| PCM | Root 14 | 0.0040 | 0.0004 | 0.0006 | 0.4354 | 0.3946 | O2-2s |
| PCM | Root 15 | 0.0030 | 0.0208 | 0.3887 | 0.3305 | 0.3847 | O1-2s |

1.4 Protonated Glycine - Gas and PCM

| Phase | Basis | N | C1 | C2 | O1 | O2 | Dominating AO |
|-------|---------|--------|--------|--------|--------|--------|---------------|
| Gas | Root 12 | 0.0315 | 0.5534 | 0.0827 | 0.0195 | 0.0096 | C1-2s |
| Gas | Root 13 | 0.3070 | 0.0353 | 0.0259 | 0.3759 | 0.1339 | O1-2s |
| Gas | Root 14 | 0.4879 | 0.0766 | 0.0145 | 0.1486 | 0.1755 | N-2s |
| Gas | Root 15 | 0.0114 | 0.0240 | 0.3302 | 0.2222 | 0.5094 | O2-2s |
| PCM | Root 12 | 0.0279 | 0.5262 | 0.1099 | 0.0214 | 0.0089 | C1-2s |
| PCM | Root 13 | 0.7342 | 0.0970 | 0.0014 | 0.0735 | 0.0071 | N-2s |
| PCM | Root 14 | 0.0698 | 0.0159 | 0.0521 | 0.4853 | 0.2587 | O1-2s |
| PCM | Root 15 | 0.0045 | 0.0163 | 0.3074 | 0.1954 | 0.5589 | O2-2s |

2 Alanine Mulliken Spin Populations

Note: O9 is the carbonyl O of COOH group, whereas O10 is the hydroxyl O of COOH group in all form of alanine.

2.1 Alanine Neutral - Gas and PCM

| Phase | N1 | C5 | O9 | O10 | Dominating AO |
|-------|--------|--------|--------|--------|---------------|
| Gas | 0.6360 | 0.0068 | 0.0110 | 0.0006 | N-2s |
| Gas | 0.0023 | 0.0568 | 0.5476 | 0.2656 | O9-2s |
| Gas | 0.0009 | 0.2926 | 0.1989 | 0.5583 | O10-2s |
| PCM | 0.5992 | 0.0125 | 0.0088 | 0.0009 | N-2s |
| PCM | 0.0012 | 0.0500 | 0.5414 | 0.2793 | O9-2s |
| PCM | 0.0006 | 0.2920 | 0.2135 | 0.5467 | O10-2s |

2.2 Alanine Zwitterion - Gas and PCM

| Phase | N | C5 | O9 | O10 | Dominating AO |
|-------|--------|--------|--------|--------|---------------|
| Gas | 0.0111 | 0.0008 | 0.4032 | 0.4011 | O9-2s |
| Gas | 0.4194 | 0.1675 | 0.1358 | 0.2236 | N-2s |
| Gas | 0.3703 | 0.2424 | 0.2278 | 0.1290 | O10-2s |
| PCM | 0.0388 | 0.0018 | 0.3878 | 0.3927 | O9-2s |
| PCM | 0.6715 | 0.0308 | 0.0083 | 0.1242 | N-2s |
| PCM | 0.0868 | 0.3703 | 0.3788 | 0.2430 | O10-2s |

2.3 Deprotonated Alanine - Gas and PCM

| Phase | N1 | C5 | O9 | O10 | Dominating AO |
|-------|--------|---------|--------|--------|---------------|
| Gas | 0.6396 | -0.0007 | 0.0569 | 0.0010 | N-2s |
| Gas | 0.0305 | 0.0000 | 0.3688 | 0.4240 | O10-2s |
| Gas | 0.0089 | 0.3997 | 0.3490 | 0.3444 | O9-2s |
| PCM | 0.6709 | -0.0003 | 0.0221 | 0.0008 | N-2s |
| PCM | 0.0051 | 0.0065 | 0.3212 | 0.5006 | O10-2s |
| PCM | 0.0065 | 0.3882 | 0.4407 | 0.2648 | O9-2s |

2.4 Protonated Alanine - Gas and PCM

| Phase | N1 | C5 | O9 | O10 | Dominating AO |
|-------|--------|---------|--------|--------|---------------|
| Gas | 0.5483 | 0.0105 | 0.2095 | 0.0518 | N-2s |
| Gas | 0.2413 | 0.0283 | 0.3115 | 0.2577 | O9-2s |
| Gas | 0.0089 | 0.3286 | 0.2265 | 0.5075 | O10-2s |
| PCM | 0.7623 | -0.0007 | 0.0375 | 0.0016 | N-2s |
| PCM | 0.0279 | 0.0287 | 0.4563 | 0.3404 | O9-2s |
| PCM | 0.0049 | 0.3315 | 0.2648 | 0.4759 | O10-2s |

3 All CAS involved Molecular Orbitals (MO) for Neutral Glycine

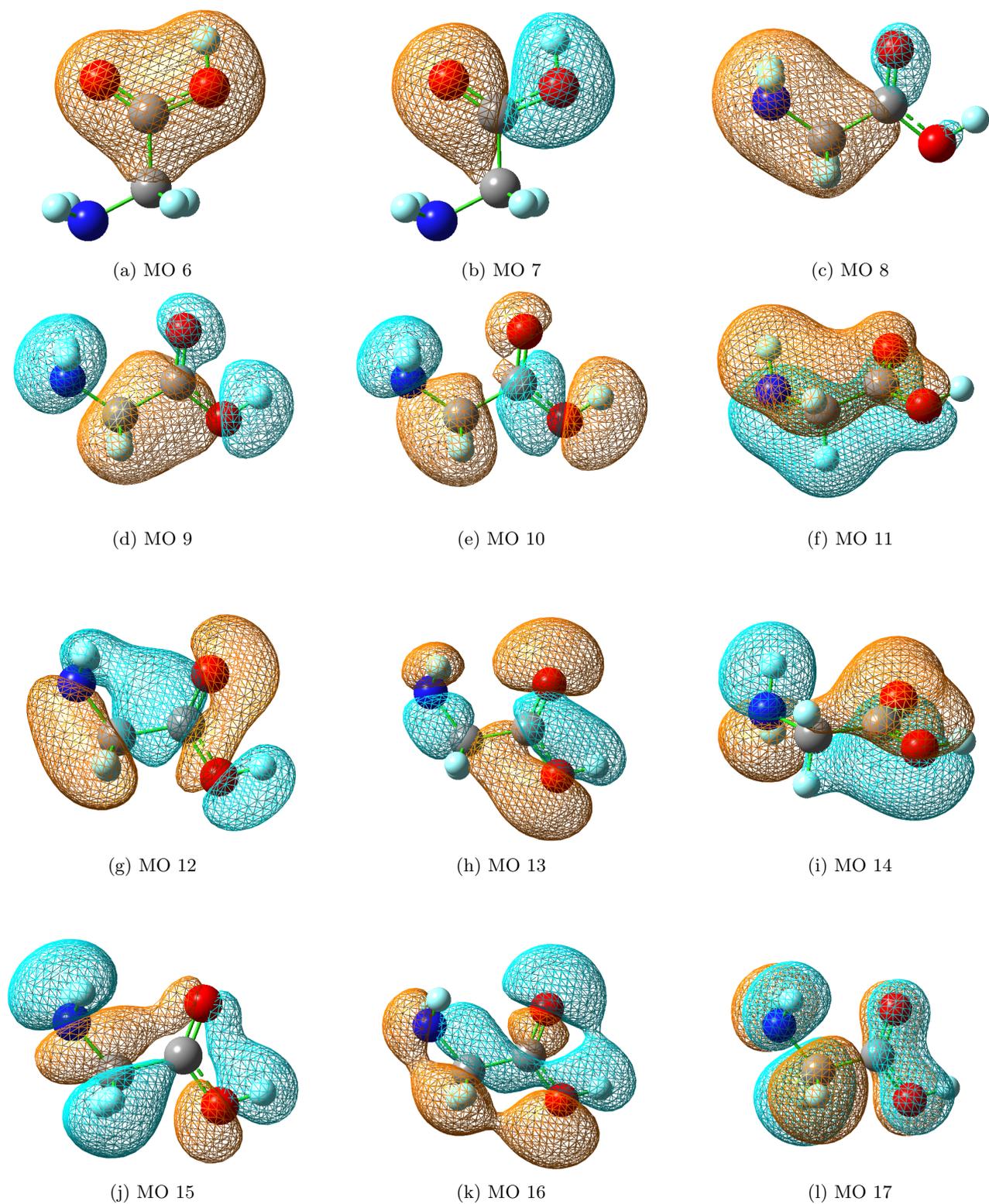
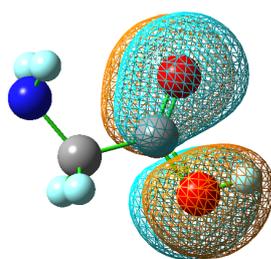
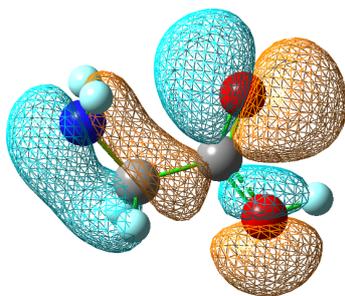


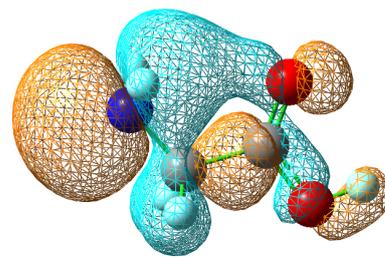
Figure 1: Molecular Orbitals 6–17 for Neutral Glycine.



(a) MO 18



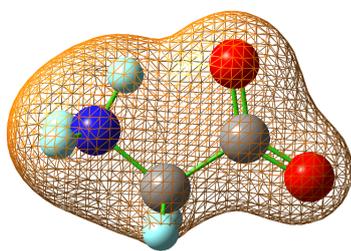
(b) MO 19



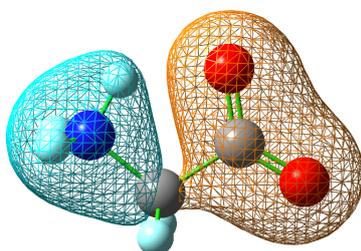
(c) MO 20

Figure 2: Molecular Orbitals 18-20 for Neutral Glycine.

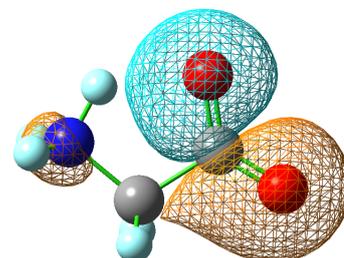
4 All CAS involved Molecular Orbitals (MO) for Zwitterion Glycine



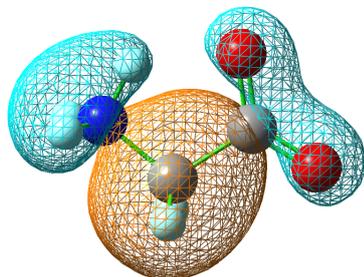
(a) MO 6



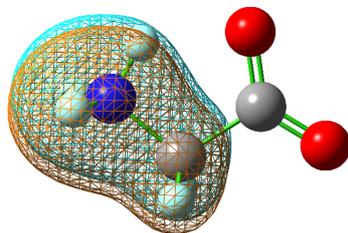
(b) MO 7



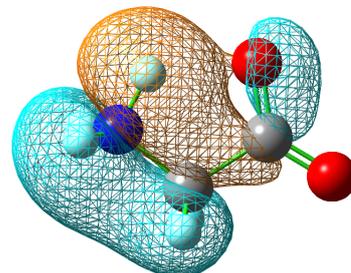
(c) MO 8



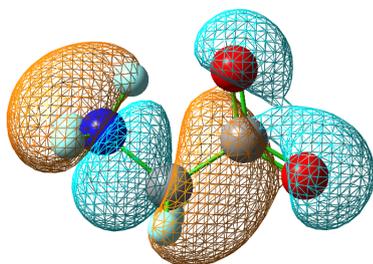
(d) MO 9



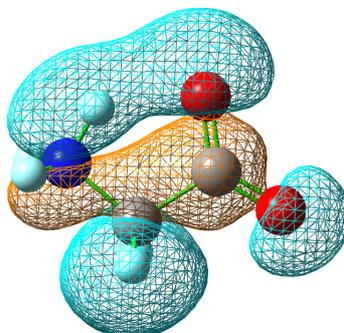
(e) MO 10



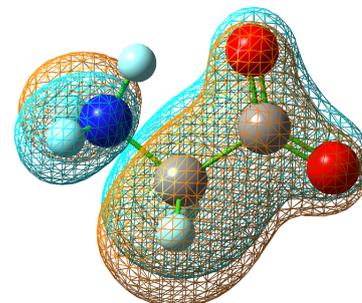
(f) MO 11



(g) MO 12



(h) MO 13



(i) MO 14

Figure 3: Molecular Orbitals 6-14 for Zwitterion Glycine.

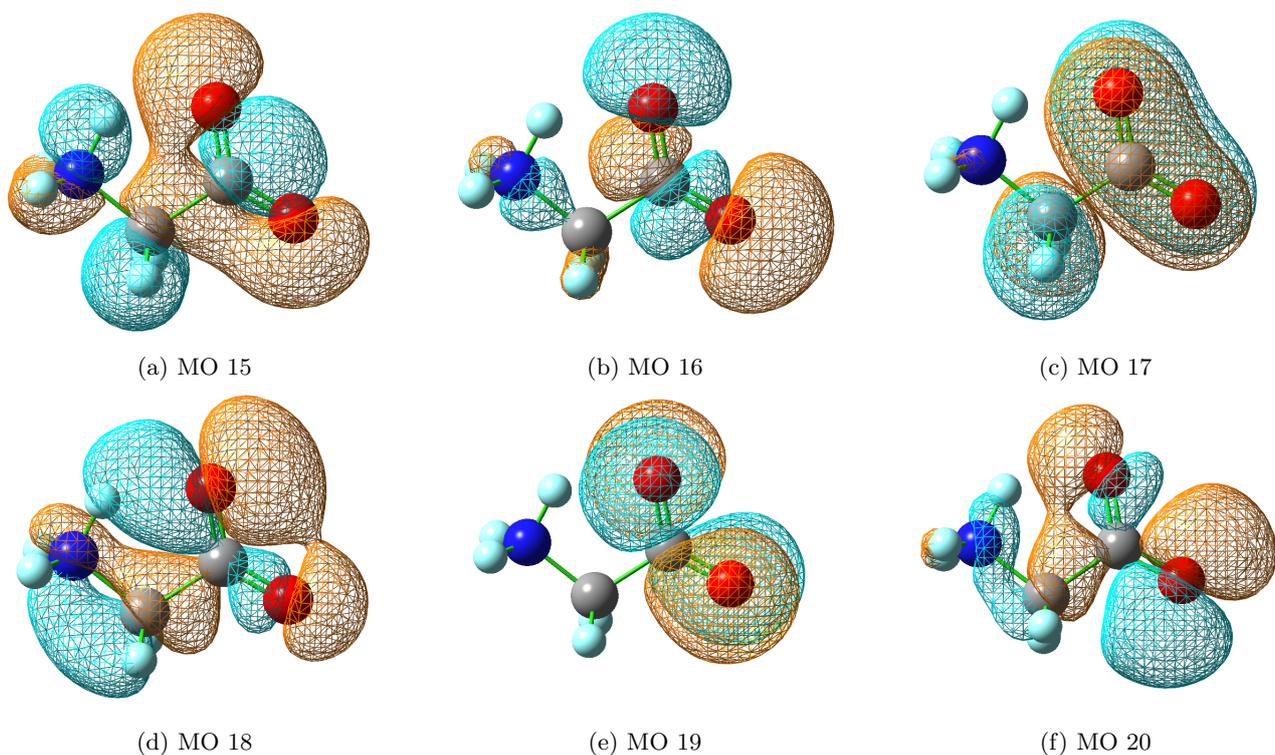


Figure 4: Molecular Orbitals 15–20 for Zwitterion Glycine.

5 All CAS involved Molecular Orbitals (MO) for Deprotonated Glycine

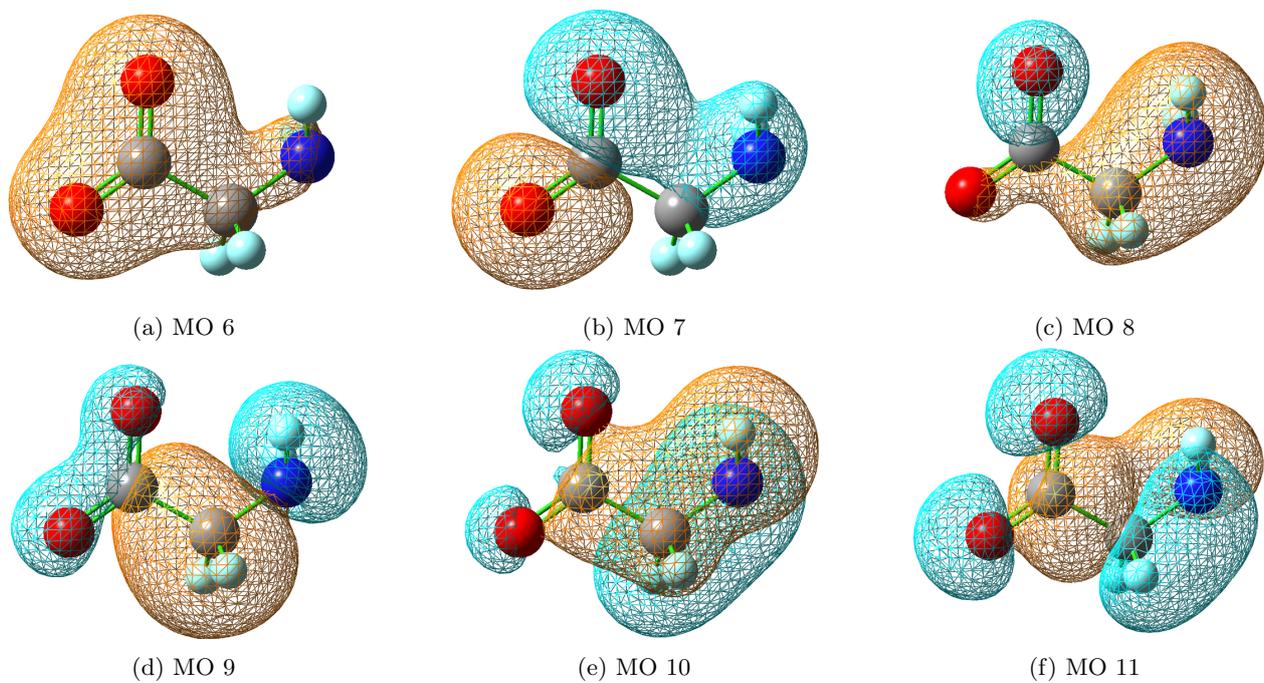


Figure 5: Molecular Orbitals 6–11 for Deprotonated Glycine.

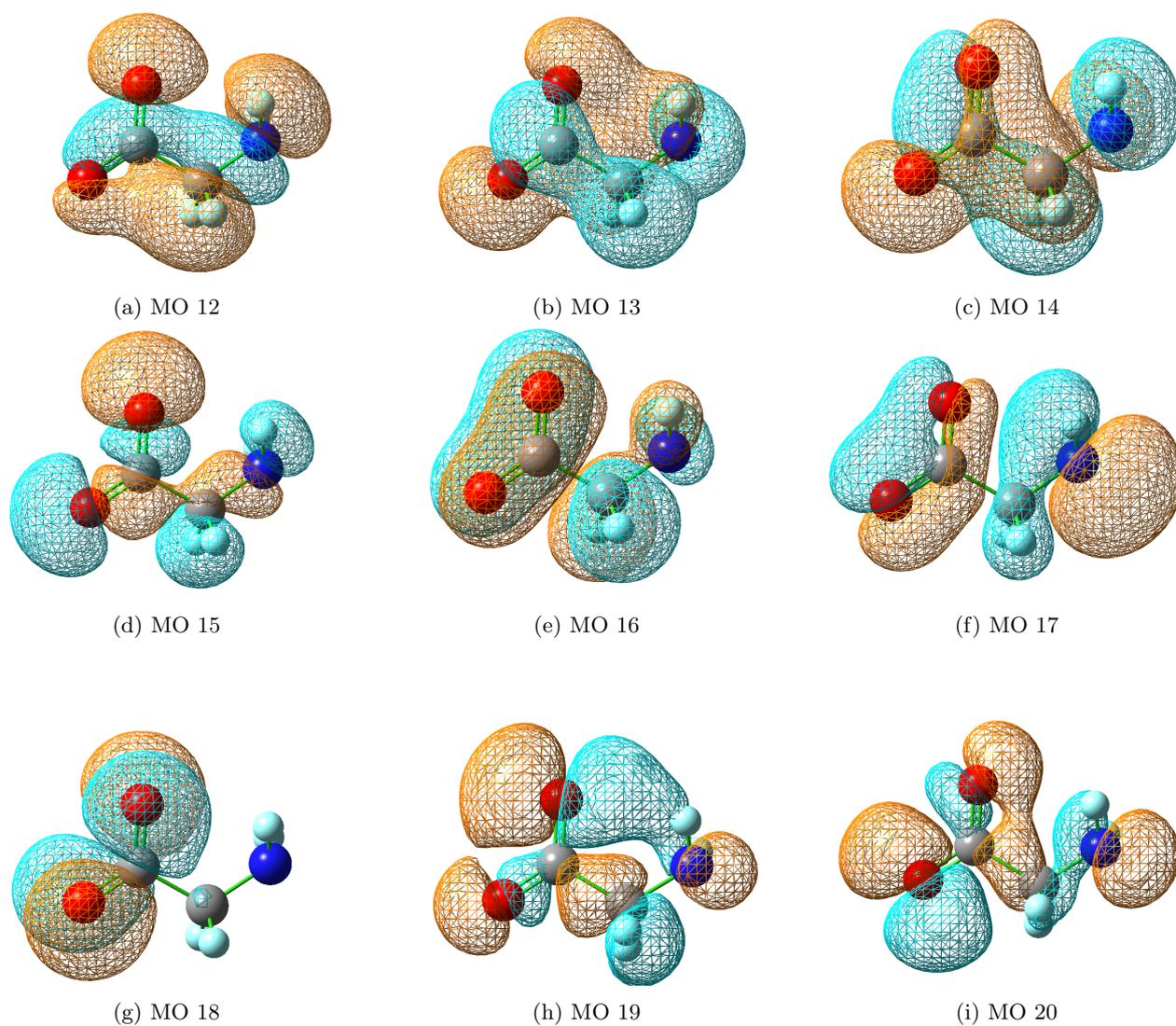


Figure 6: Molecular Orbitals 12-20 for Deprotonated Glycine.

6 All CAS involved Molecular Orbitals (MO) for Protonated Glycine

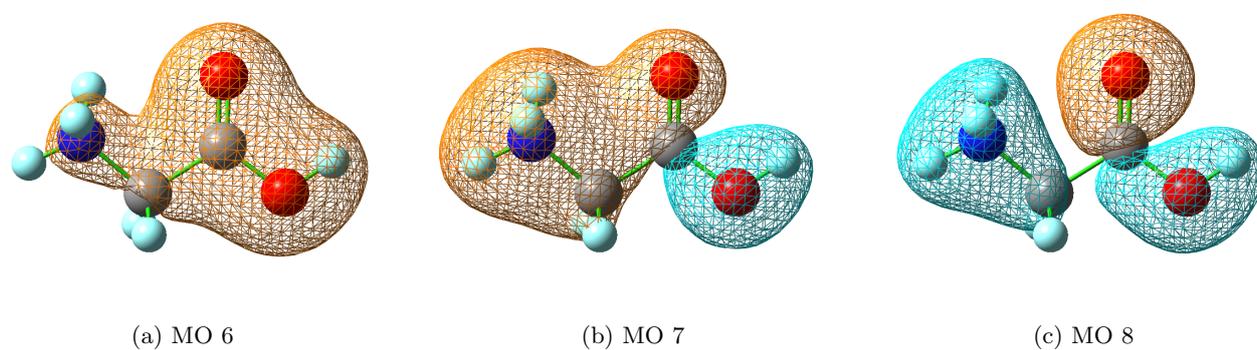
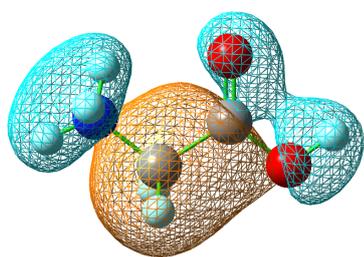
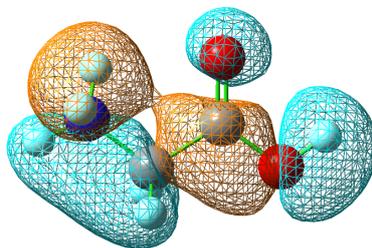


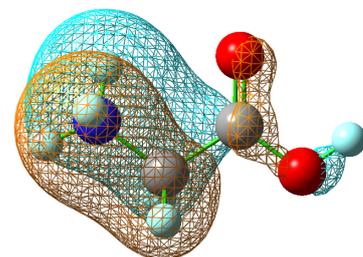
Figure 7: Molecular Orbitals 6-8 for Protonated Glycine.



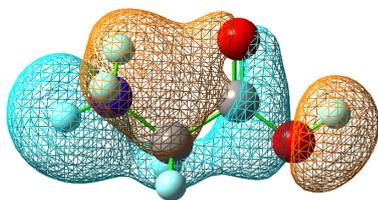
(a) MO 9



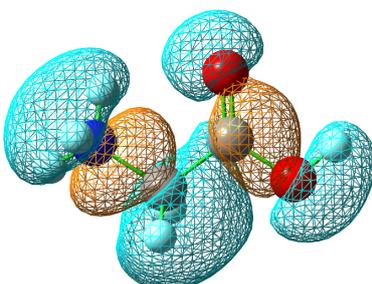
(b) MO 10



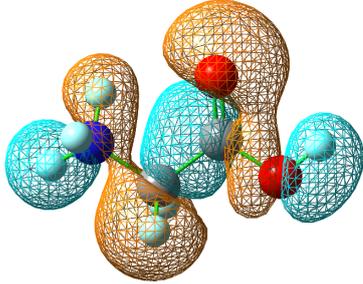
(c) MO 11



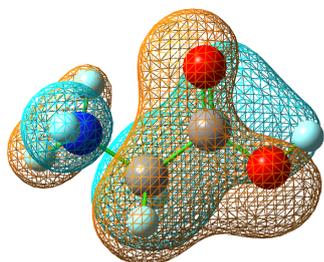
(d) MO 12



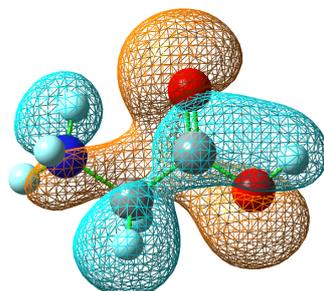
(e) MO 13



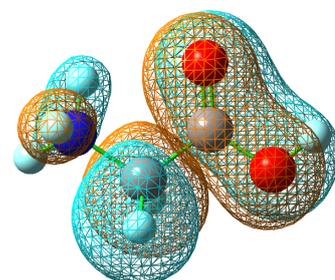
(f) MO 14



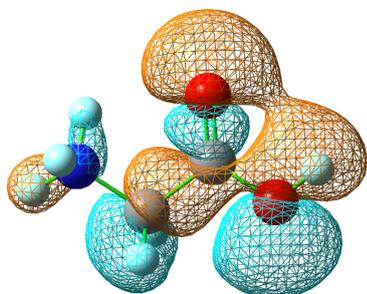
(g) MO 15



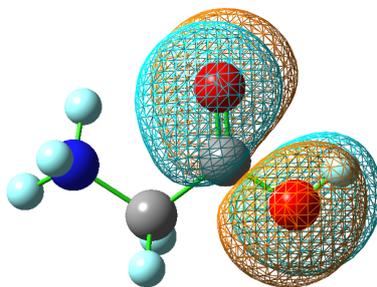
(h) MO 16



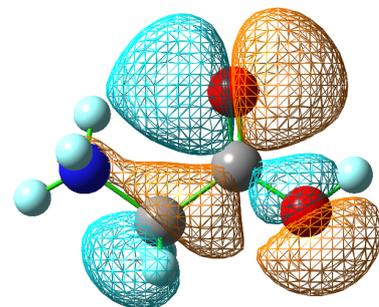
(i) MO 17



(j) MO 18



(k) MO 19



(l) MO 20

Figure 8: Molecular Orbitals 9–20 for Protonated Glycine.

7 All CAS involved Molecular Orbitals (MOs) for Neutral Alanine



Figure 9: Molecular Orbitals 7–21 for Neutral Alanine.

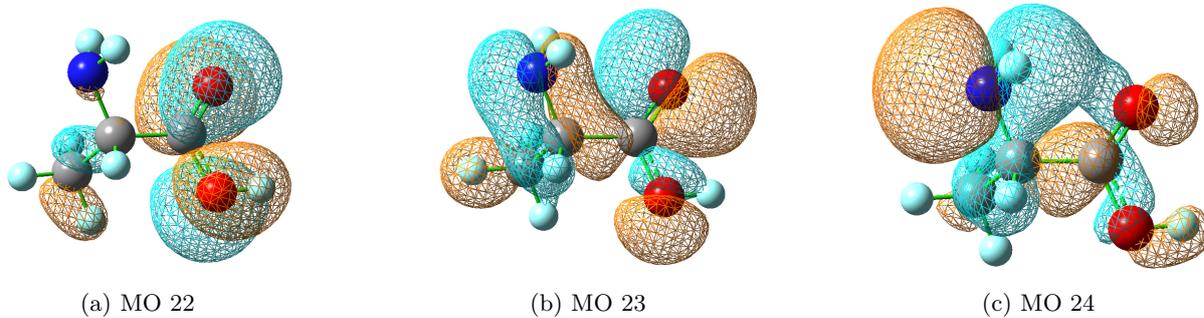


Figure 10: Molecular Orbitals 22–24 for Neutral Alanine.

8 All CAS-involved molecular orbitals (MOs) for zwitterionic alanine.

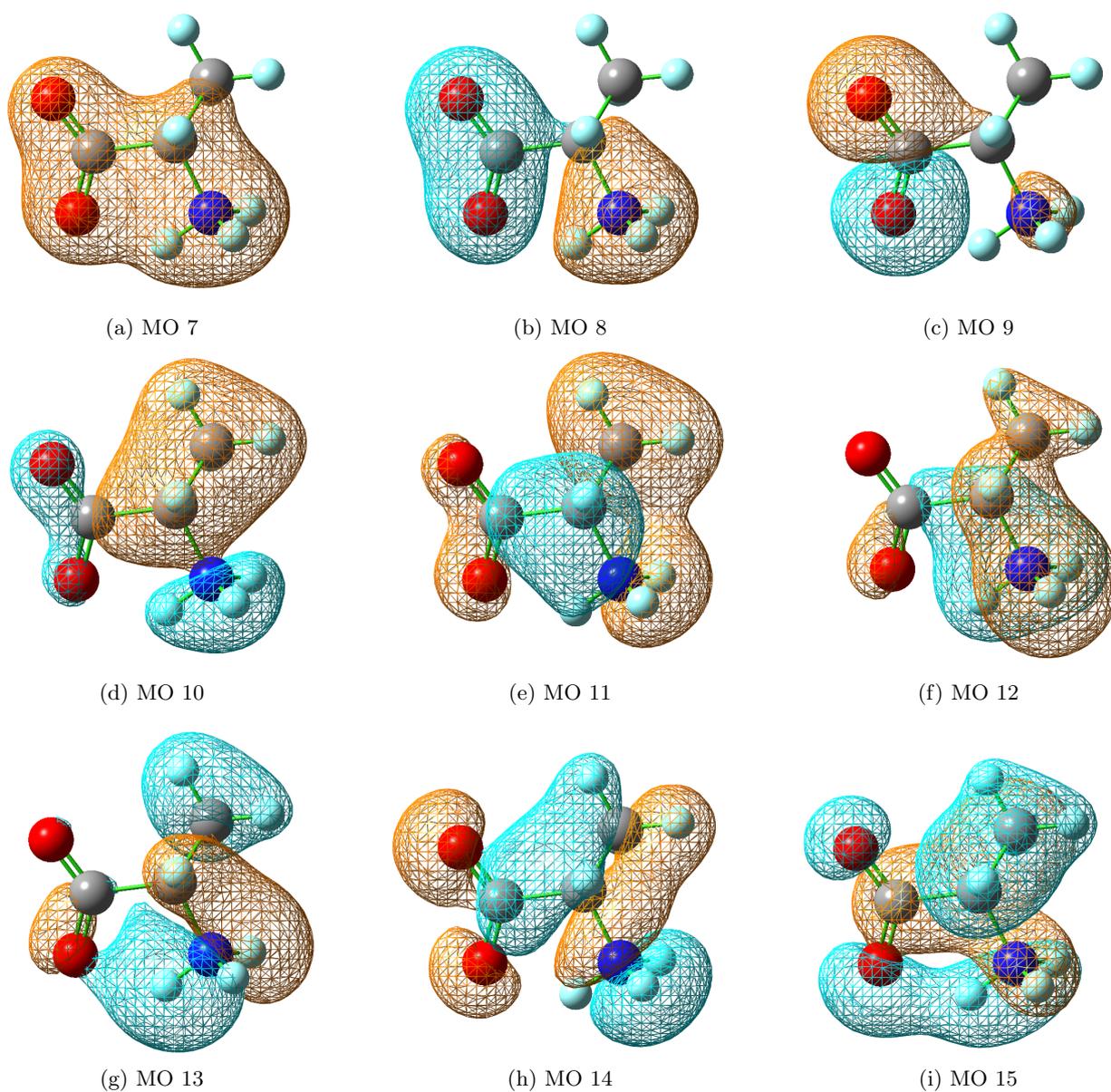


Figure 11: Molecular Orbitals 7–15 for Zwitterionic Alanine.

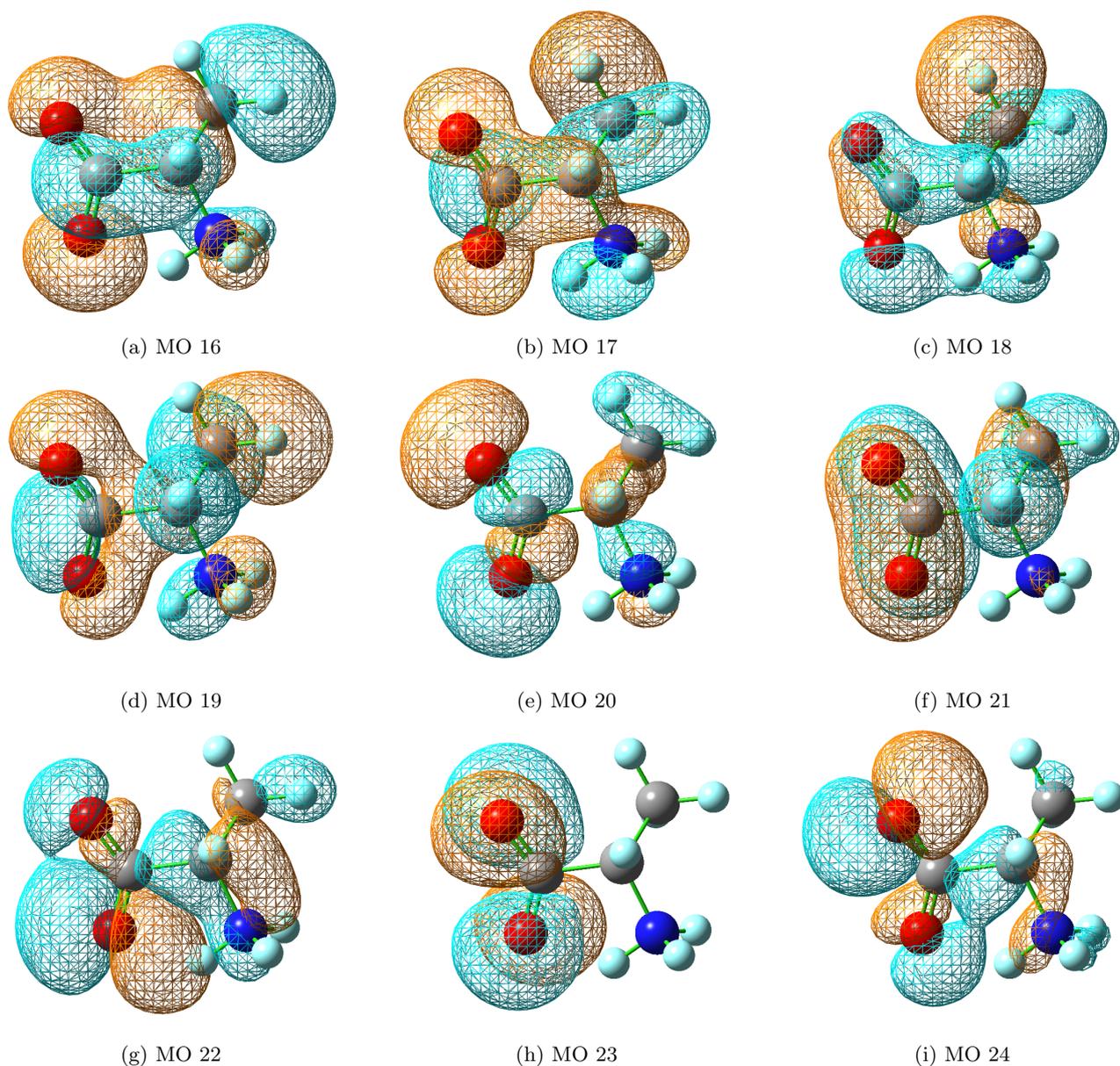


Figure 12: Molecular Orbitals 16–24 for zwitter Alanine.

9 All CAS involved Molecular Orbitals (MOs) for Deprotonated Alanine

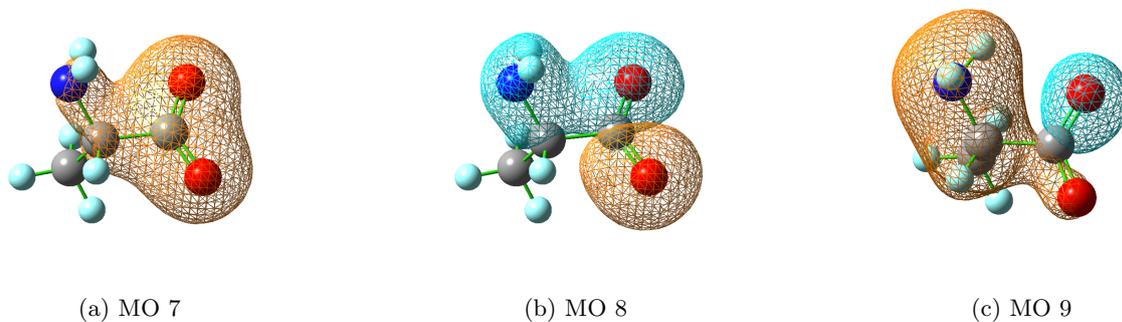


Figure 13: Molecular Orbitals 7–9 for Deprotonated Alanine.

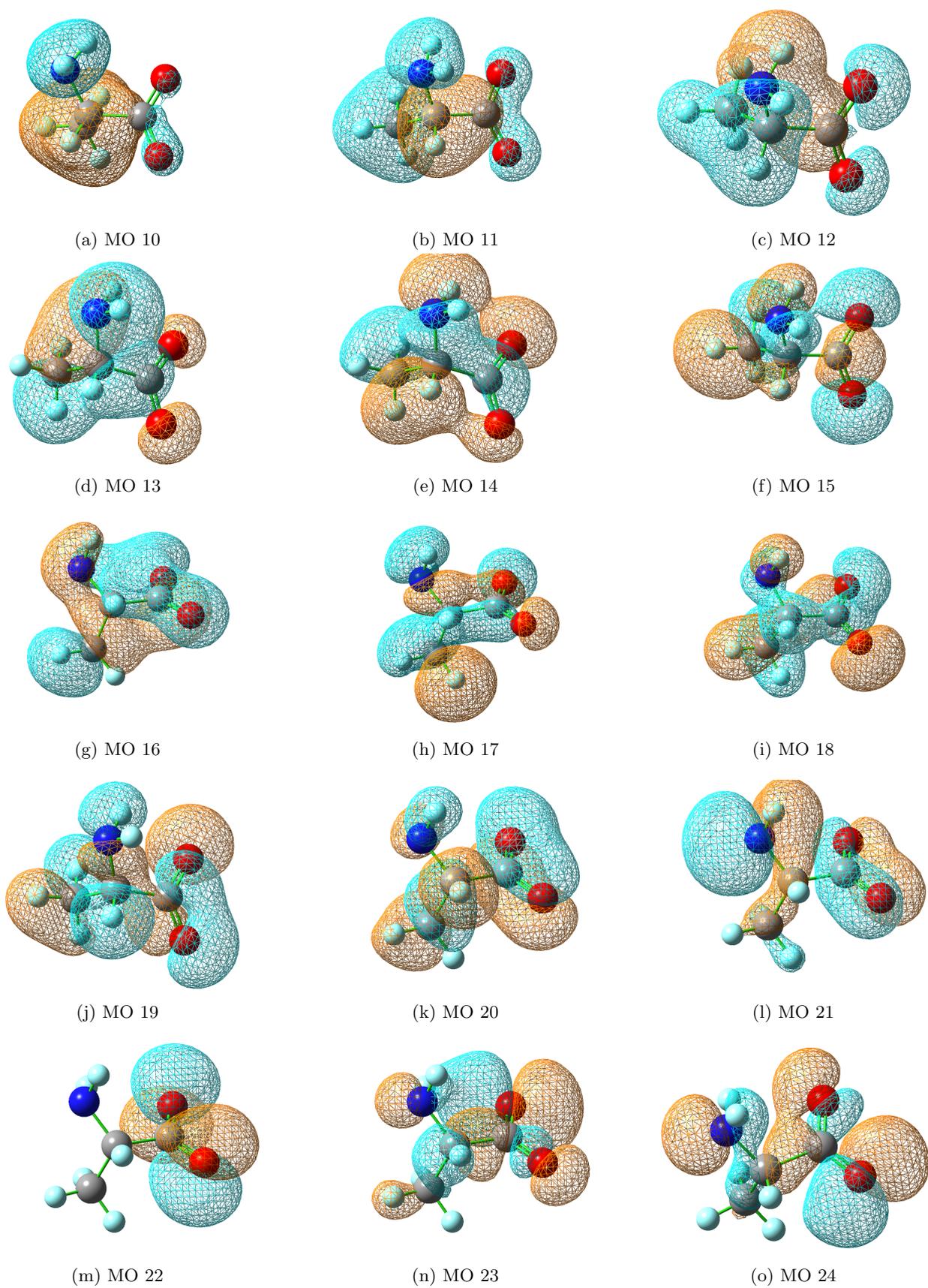


Figure 14: Molecular Orbitals 10–24 for deprotonated Alanine.

10 All CAS involved Molecular Orbitals (MOs) for Protonated Alanine

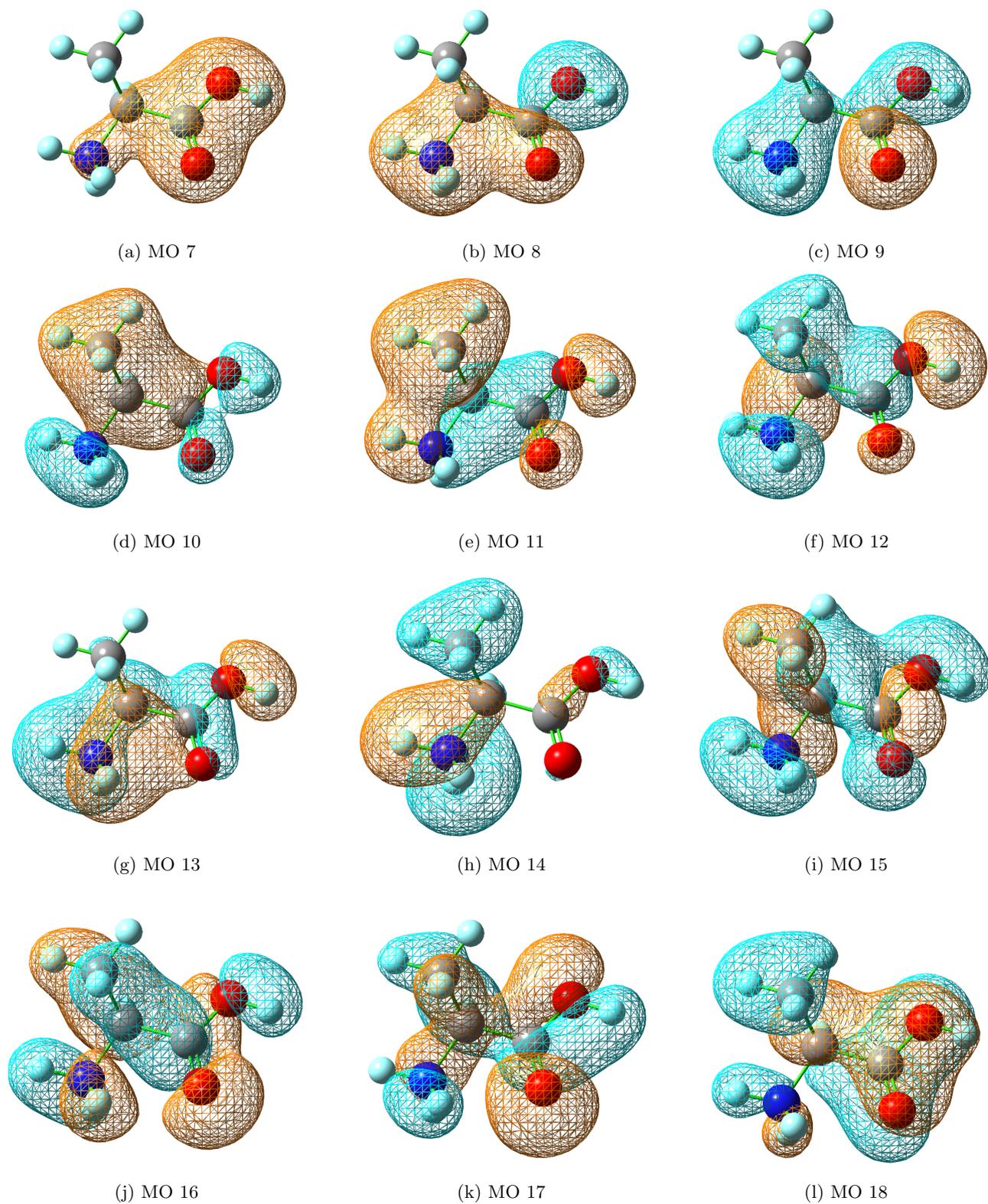
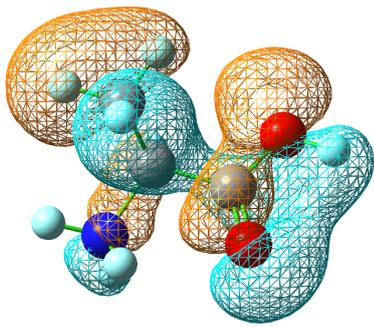
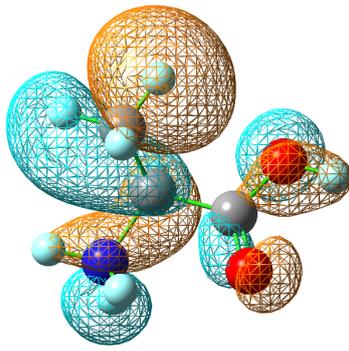


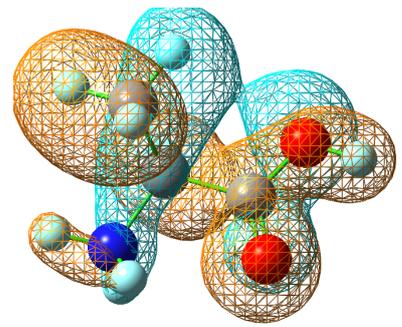
Figure 15: Molecular Orbitals 7–18 for Protonated Alanine.



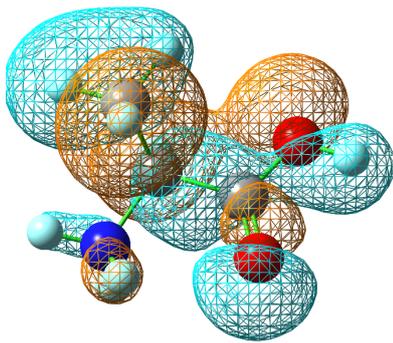
(a) MO 19



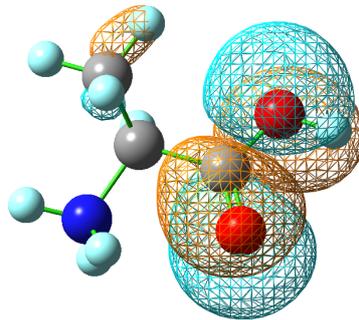
(b) MO 20



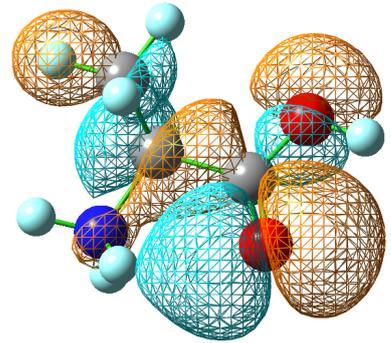
(c) MO 21



(d) MO 22



(e) MO 23



(f) MO 24

Figure 16: Molecular Orbitals 19–24 for Protonated Alanine.