Intermediate Neglect Differential Overlap (INDO)/BG

The INDO/BG method was simultaneously published with the respective Complete Neglect Differential Overlap (CNDO)/BG variant (*1, 2*). The two methods are quite similar, except for differences in the Fock matrix itself. INDO/BG uses different values for $U_{\mu\mu}^{A,eff}$ and for the Coulomb integrals. Just as in Pople's INDO method, exchange integrals are estimated for orbitals in the same atom. Due to the similarity between the BG methods, we will solely focus on the differences between INDO/BG and CNDO/BG.

The Fock matrix for closed-shell systems is given by (highlighted with yellow the INDO terms)

$$F_{\mu\mu}^{AA} = H_{\mu\mu} + \sum\nolimits_{\lambda} P_{\lambda\lambda}\,(\mu\mu|\lambda\lambda) - \frac{1}{2}P_{\mu\mu}\,(\mu\mu|\mu\mu) \boxed{-\frac{1}{2}\sum\nolimits_{\lambda\in A}^{\lambda\neq\mu} P_{\lambda\lambda}\,(\mu\lambda|\mu\lambda)} \tag{1}$$

$$F_{\mu\nu}^{AB} = H_{\mu\mu} - \frac{1}{2}P_{\mu\nu}\,(\mu\mu|\nu\nu) \boxed{+\frac{3}{2}P_{\mu\nu}\,(\mu\lambda|\mu\lambda)\,\delta_{AB}} \tag{2}$$

whereas for open-shells

$$F_{\mu\mu}^{AA,\delta} = H_{\mu\mu} + \sum\nolimits_{\lambda} P_{\lambda\lambda}\,(\mu\mu|\lambda\lambda) - P_{\mu\mu}^{\delta}\,(\mu\mu|\mu\mu) \boxed{-\sum\nolimits_{\lambda\in A}^{\lambda\neq\mu} P_{\lambda\lambda}^{\delta}\,(\mu\lambda|\mu\lambda)} \tag{3}$$

$$F_{\mu\nu}^{AB,\delta} = H_{\mu\mu} - P_{\mu\nu}^{\delta}\,(\mu\mu|\nu\nu) \boxed{+\left(2P_{\mu\nu} - P_{\mu\nu}^{\delta}\right)(\mu\lambda|\mu\lambda)\,\delta_{AB}} \tag{4}$$

Note that as the Fock matrix elements were written, it is possible that atoms A and B be the same. That is why we multiplied the respective INDO terms by δ_{AB}. Even though the integrals $(\mu\lambda|\mu\lambda)$ are by definition one-center only, this notation becomes clearer.

The core Hamiltonian required to build the Fock matrix is calculated exactly as in CNDO/BG. Elements $U_{\mu\mu}^{A,eff}$ and $J_{\mu\nu}^{AA}$ are however calculated differently.

Coulomb integrals are given by

$$\begin{aligned}
J_{ss}^{AA} &= F_0^{ss} \\
J_{sp}^{AA} &= F_0^{sp} = J_{ps}^{AA} \\
J_{sd}^{AA} &= F_0^{sd} = J_{ds}^{AA} \\
J_{pd}^{AA} &= F_0^{pd} = J_{dp}^{AA} \\
\boxed{J_{p_\alpha p_\alpha}^{AA} &= F_0^{pp} + 4F_2^{pp}} \\
\boxed{J_{p_\alpha p_\beta}^{AA} &= F_0^{pp} - 2F_2^{pp}} \\
\boxed{J_{d_\alpha d_\alpha}^{AA} &= F_0^{dd} + 4F_2^{dd} + 36F_4^{dd}} \\
\boxed{J_{d_\alpha d_\beta}^{AA} &= F_0^{dd} - F_2^{dd} - 9F_4^{dd}}
\end{aligned} \tag{5}$$

In the above integrals, p_α, p_β, d_α and d_β represent orbitals of a given azimuthal quantum number (p or d) with different magnetic quantum numbers. Values for F_2^{pp}, F_2^{dd} and F_4^{dd} are also tabulated.

Table 1: F_2^{dd}, F_4^{dd}, G_2^{sd}, G_1^{pd} and G_3^{pd} as given in (*1, 2*). All values in cm^{-1}.

	F_2^{dd}	F_4^{dd}	G_2^{sd}	G_1^{pd}	G_3^{pd}
K	199	5	488	238	5
Ca	400	10	746	364	8
Sc	745	53.5	1957	420	15.7
Ti	875	63	2000	450	16.8
V	1005	72.5	2100	480	17.9
Cr	1135	82	2100	510	19.1
Mn	1265	91.5	1900	540	20.2
Fe	1395	101	1800	570	21.3
Co	1525	1105	2100	600	22.4
Ni	1655	120	2000	630	23.5
Cu	1785	129.5	2300	660	24.6
Zn	1915	139	2118	690	25.7

Finally one must still define the exchange integrals, which in INDO/BG are also defined from spectroscopic data. The following exchange integrals are required by the method:

$$\begin{aligned}
(sp|sp) = (ps|ps) &= G_1^{sp} \\
(sd|sd) = (ds|ds) &= G_2^{sd} \\
(p_\alpha p_\beta|p_\alpha p_\beta) = (p_\beta p_\alpha|p_\beta p_\alpha) &= 3F_2^{pp} \\
(pd|pd) = (dp|dp) &= 2G_1^{pd} + 21G_3^{pd} \\
(d_\alpha d_\beta|d_\alpha d_\beta) = (d_\beta d_\alpha|d_\beta d_\alpha) &= 2.5F_2^{dd} + 22.5F_4^{dd}
\end{aligned} \tag{6}$$

Table 2: $U^A_{\mu\mu}$ (eV) and F^{pp}_2 (cm^{-1}) used in INDO/BG, as given in (*1, 2*).

	U^A_{ss}	U^A_{pp}	U^A_{dd}	F^{pp}_2	G^{sp}_1
H	-12.575	—	—	—	—
Li	-4.905	-3.603	—	426	6735
Be	-15.123	-11.948	—	857	10292
B	-29.308	-23.837	—	1123	14522
C	-48.507	-39.744	—	1455	18545
N	-66.518	-54.898	—	2084	24085
O	-95.329	-79.311	—	2227	31766
F	-120.865	-101.634	—	2774	38963
Na	-4.254	-3.068	—	196	4188
Mg	-12.298	-9.027	—	1056	6658
Al	-21.344	-17.384	—	517	9031
Si	-33.939	-28.249	—	730	12938
P	-52.013	-39.137	—	951	2817
S	-61.452	-53.367	—	1464	8269
Cl	-79.398	-69.248	—	2056	10142
K	-2.378	-1.869	-3.032	46	2745
Ca	-7.382	-4.618	-7.159	93	4195
Sc	-15.675	-9.804	-23.270	330	2250
Ti	-22.650	-14.352	-36.369	350	2400
V	-30.015	-19.158	-50.651	370	2550
Cr	-37.770	-24.222	-66.118	390	2700
Mn	-45.915	-29.544	-82.773	410	2850
Fe	-54.450	-35.124	-100.615	430	3000
Co	-63.375	-40.962	-119.648	450	3150
Ni	-72.690	-47.058	-139.871	470	3300
Cu	-81.645	-53.412	-161.287	490	3450
Zn	-92.475	-60.00	-183.917	510	3600

Even though INDO theories are more evolved and complete than the respective CNDO methods (the CNDO and INDO methods of Pople, for instance, are very close to each other, but the latter can treat more accurately singlet-triplet splittings), in the case of INDO/BG, since there are no parameters for d orbitals in third-row elements, the method

is restricted to describe systems of third-row elements that are not using d orbitals. This means that the connectivity is restricted to 4 chemical bonds.

Bibliography

1. M. C. Böhm and R. Gleiter *Theor. Chim. Acta (Berl.)*, vol. 59, p. 127, 1981.

2. M. C. Böhm and R. Gleiter *Theor. Chim. Acta (Berl.)*, vol. 59, p. 153, 1981.