Charge Iteration in **bind**

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0.1 Goals and Problems

The basic idea of charge iteration is to use calculated charges to adjust the diagonal elements of the hamiltonian (the H_{ii}'s) in a self-consistent manner. The main reason I see for doing this is to have parameters that are reasonable for a given system that are generated in a well defined manner (instead of having a different *ad hoc* set of parameters for every calculation). The way this is done is using the equation:

$$H_{ii}^{(k+1)} = A(Q^{(k)})^2 + BQ^{(k)} + C \qquad (0.1)$$

where $H_{ii}^{(k+1)}$ is the new value of H_{ii} for step $k+1$, A, B and C are parameters and $Q^{(k)}$ is the net charge on the atom calculated using the value of $H_{ii}^{(k)}$.

The traditional problem with charge iteration, as I see it, is that the self consistent calculations do not always converge in a timely fashion. Some don't converge at all. Since the form of the expression for $H_{ii}^{(k+1)}$ (Equation 0.1) seems simple and unlikely to lead to numeric explosions, I would say that the convergence problems may be due to the implementation of the charge iteration procedure.

For the sake of clarity (and because I haven't implemented the other scheme), I'm going to limit myself to only discussing charge iteration using a single configuration (a single set of parameters).

0.2 The Old Way

The implementation of charge iteration in ICON, which is what we've used, is pretty complicated. Here's how it works.

The underlying form is that of equation 0.1, but the calculation of the value of Q is complicated. First of all, the occupancy of each orbital (p_i where i indexes the orbital) is calculated using a damping scheme:

$$p_i^{(k+1)}(initial) = p_i^{(k)}(initial) + \lambda \Delta p_i^{(k)} \qquad (0.2)$$

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again i indexes the orbital, k indicates which step we're on, $(initial)$ refers to the occupancy at the beginning of the step (not the occupancy calculated using the results from this step), λ is a step size, and $\Delta p_i^{(k)}$ is defined as:

$$\Delta p_i^{(k)} = p_i^{(k)}(final) - p_i^{(k)}(initial) \tag{0.3}$$

In equation 0.3 $(final)$ refers to the orbital occupancy which was calculated in this step.

These orbital occupancies are used to calculate the net charge on each atom ν:

$$Q_\nu^{(k+1)} = \sum_{i \ on \ \nu} p_i^{(k+1)}(initial) \tag{0.4}$$

and these $Q_\nu^{(k+1)}$'s are used to generate the $H_{ii}^{(k+1)}$'s:

$$H_{ii}^{(k+1)} = A_i(Q_\nu^{(k+1)})^2 + B_i Q_\nu^{(k+1)} + C_i \tag{0.5}$$

The new $H_{ii}^{(k+1)}$'s are used to generate a new hamiltonian and the process repeats until some convergence criterion is met.

The presence of the λ (step size) in equation 0.2 is to provide some damping for the adjustment (note that $\lambda < 1$). This lessens problems with H_{ii} values "sloshing" between 2 values. In ICON, the value of λ is adjusted as the calculation proceeds. This is supposed to speed convergence. The formula for adjusting λ is fairly complicated, so I'm not going to go into it here.

0.3   The New Way

The way charge iteration is currently done in bind is a lot simpler and it doesn't seem to have bad convergence problems (of course, it hasn't been extensively tested yet). I've taken a very "first order" approach. Instead of damping the changes in orbital occupations, I damp the changes in H_{ii}. So the orbital occupations are not played around with, i.e.:

$$p_i^{(k+1)}(initial) = p_i^{(k)}(final) \tag{0.6}$$

Equation 0.4 is still used to generate the net charges. Then, an undamped new value of H_{ii} is calculated:

$$H_{ii}{}' = A_i(Q_\nu^{(k+1)})^2 + B_i Q_\nu^{(k+1)} + C_i \tag{0.7}$$

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and $H_{ii}^{(k+1)}$ is calculated as follows:

$$H_{ii}^{(k+1)} = H_{ii}^{(k)} + \lambda(H_{ii}^{(k)'} - H_{ii}^{(k)}) \tag{0.8}$$

That's it. It's very first order, but it seems to work reasonably well. It's worth testing this whole thing some more.