**Unconstrained Two-Vector Algorithm for Constrained Energy Minimization (Last updated 7/18)**

This document describes a QEq algorithm using two kinds of fictitious charge under charge-neutrality constraint.

* Two-vector algorithm

 (2)

 (1)

with charge-neutrality constraint,



To solve this problem, use Lagrange multiplier method minimizing the electrostatic energy without constraint,



or,



To determine , multiply to the Equation (7),



Taking summation with index *k,*





Introduce two fictitious charge *s* and *t*. Eq. (8) can be rewritten as



or,

Eq. (12) and (13) are equivalent to unconstrained minimization of the following quadratic functions,



which can be solved with conjugate gradient with gradients,



The real charge becomes the combination of *s* and *t*.



which is identical to Eq.(7). Therefore,

is the solution of the original problem.

* Line minimization

The line minimization coefficient can be obtained from the second order Taylor expansion of quadratic functions,



where *g* is gradient, *H* is Hessian and *h* is conjugate direction. Define the line minimization coefficient and residual energy as,



* Subroutines
* qeq\_initialize()

Notice that the second term in the Hessian matrix in Eq.(2) only depends on atomic coordinate. Storing this invariant and reusing it during iteration significantly reduces the total computation time of QEq subroutine. Use *A0(j,i)* to store the Hessian component,



Note: The order of indices of *A0* is intentionally swapped considering memory access pattern.

* get\_gradient()

Compute gradients for *s* and *t* vectors and dot product of gradient vectors to update conjugate direction. From Eq.(2) and Eq.(16),



Define variables in code,



The gradients and new conjugate direction factors are respectively,





* get\_hsh()

Compute for the line minimization coefficient in Eq.(19) and the electrostatic energy *Est* to check the convergence. From Eq.(2),



Variables are defined in code as,



* QEq()

Main QEq routine. The electronegativity, line minimization coefficient *lmin* and Fletcher-Reeves conjugate direction factor are calculated here. Variables are defined as,

 

* qeq\_finalize()

Reallocate all of variables.