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REGULAR ARTICLE

Self-consistent methods constrained to a fixed number of particles in a given fragment and its relation to the electronegativity equalization method

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Abstract The variational procedure of the Hartree–Fock and Kohn–Sham methods can be modified by adding one or more constraints that fix the number of electrons in a given number of molecular fragments. The corresponding Euler–Lagrange equations lead to a modified Fock matrix, where the contribution from the constraints only depends on the overlap matrix, when using the Mulliken or Hirshfeld atoms-in-molecules method. For all compounds in the test set, the energy shows a quadratic dependence on the fixed charges. This behavior provides a procedure to obtain the atomic electronegativity and hardness parameters in the electronegativity equalization method.

Keywords Hartree–Fock method · Kohn–Sham method · Mulliken population analysis · Electronegativity equalization method · Atomic charges

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1 Introduction

The way the electrons distribute in a molecule reflects its physical and chemical properties. For example, dipole moments and electron deficient sites are relevant properties in a molecule that affect the way it interacts with the reaction partners, and these properties are determined by the molecular charge distribution. Quantum mechanics allows the computation of the electron density, which tells the way electrons distribute in the molecule. However, the electron density can only be obtained from an electronic structure computation, and simpler methods are also required to estimate the atomic charges in complex systems.

The electronegativity equalization method (EEM) [1] has been successfully used to estimate atomic charges in a wide variety of electronic systems, from simple molecules to inorganic materials [2, 3]. In EEM, a molecule is described in terms of its atoms, and the molecular energy is approximated as a quadratic function of the atomic charges. One can rationalize the EEM approach by partitioning the expectation value of the Hamiltonian operator into intra- and interatomic regions [1, 4–6]:

$$\begin{aligned}\langle\hat{H}\rangle = {} & \sum_{A}\int_{\Omega_A}\left(\left[-\frac{1}{2}\nabla^2+v(\vec{r})\right]\gamma_1(\vec{r};\vec{r}\,')\right)\Big|_{\vec{r}\,'=\vec{r}}\mathrm{d}\vec{r} \\ & +\sum_{A,B}\int_{\Omega_A}\int_{\Omega_B}\frac{\gamma_2(\vec{r}_1,\vec{r}_2;\vec{r}_1,\vec{r}_2)}{r_{12}}\mathrm{d}\vec{r}_1\mathrm{d}\vec{r}_2 \\ & +\frac{1}{2}\sum_{\substack{A,B\\(A\neq B)}}\frac{Z_A Z_B}{R_{AB}}. \qquad (1)\end{aligned}$$

Here, γ_1 and γ_2 are the one- and two-body density matrices, Ω_A represents the region of space that is allocated to atom A, and v corresponds to the electric potential from the nuclei,

$$v(\vec{r}) = \sum_A v_A(\vec{r}) = -\sum_A \frac{Z_A}{\left|\vec{r} - \vec{R}_A\right|}. \tag{2}$$

Then, one can collect the one- and two-region terms:

$$\langle \hat{H} \rangle = \sum_A E_A^* + \sum_{\substack{A,B \\ (A \neq B)}} V_{AB}^*. \tag{3}$$

where the quasi-atomic energies, E_A^*, are one-region contributions,

$$E_A^* = \int_{\Omega_A} \left\{ -\frac{1}{2} \left[\nabla^2 \gamma_1(\vec{r}; \vec{r}') \right] \Big|_{\vec{r}'=\vec{r}} + v_A(\vec{r}) \rho(\vec{r}) \right\} d\vec{r} + \int_{\Omega_A} \int_{\Omega_A} \frac{\gamma_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 \tag{4}$$

while the interatomic terms, V_{AB}^*, are two-region ones,

$$V_{AB}^* = \int_{\Omega_B} v_A(\vec{r}) \rho(\vec{r}) d\vec{r} + \int_{\Omega_A} \int_{\Omega_B} \frac{\gamma_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \frac{1}{2} \frac{Z_A Z_B}{R_{AB}}. \tag{5}$$

Note that a quasi-atomic energy is different from a free-atom energy, since it depends on the molecular density matrices. The two-body density matrix can be written in terms of the density and the pair-correlation function (h):

$$\gamma_2(\vec{r}_1, \vec{r}_2; \vec{r}_1, \vec{r}_2) = \frac{1}{2} \rho(\vec{r}_1) \rho(\vec{r}_2) [1 + h(\vec{r}_1, \vec{r}_2)], \tag{6}$$

where the pair-correlation function leads to the exchange and correlation energy contributions. From the use of a continuous representation of the nuclear density, one has that

$$V_{AB}^* + V_{BA}^* = \int_{\Omega_A} \int_{\Omega_B} \frac{\left[Z_A \delta(\vec{r}_1 - \vec{R}_A) - \rho(\vec{r}_1) \right] \left[Z_B \delta(\vec{r}_2 - \vec{R}_B) - \rho(\vec{r}_2) \right]}{r_{12}} d\vec{r}_1 d\vec{r}_2 + \int_{\Omega_A} \int_{\Omega_B} \frac{\rho(\vec{r}_1) \rho(\vec{r}_2) h(\vec{r}_1, \vec{r}_2)}{r_{12}} d\vec{r}_1 d\vec{r}_2, \tag{7}$$

where the factors inside the square brackets represent the total molecular density at a given point in space, and the first term is the Coulomb interaction between two charge densities from different regions. The Coulomb term can be computed using the multipole expansion. If one neglects the contribution of the pair-correlation function, by assuming that its effects can be partially included in the parametrization of the quasi-atomic energies, and truncates the multipole expansion up to the monopole term, then one gets a simple expression for the sum of the two-region terms:

$$\sum_{\substack{A,B \\ (A \neq B)}} V_{AB}^* \approx \frac{1}{2} \sum_{\substack{A,B \\ (A \neq B)}} \frac{q_A q_B}{R_{AB}}. \tag{8}$$

Here, q_A represents the charge of atom A.

Since, in general, the atomic charges are not an integer, a second-order Taylor expansion of the energy, around the neutral state, is usually used for the quasi-atomic energies:

$$E_A^* \approx E_A^{o*} + \chi_A^* q_A + \frac{1}{2} \eta_A^* q_A^2 \tag{9}$$

where χ_A^* and η_A^* are the quasi-atomic electronegativity and hardness. From density functional chemical reactivity theory, the electronegativity is identified as the negative of the electronic chemical potential, while the hardness represents the response of the chemical potential to the change in the number of electrons (See for example [7]). In some special cases, it could be important to change the reference point for the Taylor expansion. Such a change slightly alters the form of the quadratic expression by replacing the terms q_A by $\left(q_A - q_A^0\right)$, where, as described below, q_A^0 is the charge on atom A using the unconstrained molecular wave function.

The combination of Eqs. (3) and (8, 9) leads to the EEM master equation:

$$E_{mol} = \langle \hat{H} \rangle \approx E^{EEM} = \sum_A \left(E_A^{o*} + \chi_A^* q_A + \frac{1}{2} \eta_A^* q_A^2 \right) + \frac{1}{2} \sum_{\substack{A,B \\ (A \neq B)}} \frac{q_A q_B}{R_{AB}}. \tag{10}$$

Note that the molecular energy is approximated by a quadratic function of the atomic charges. Atomic charges come from the minimization of Eq. (10), subject to the restriction

$$0 = \sum_A q_A - Q \tag{11}$$

where Q is the charge of the molecule, which leads to the following set of equations,

$$\frac{\partial E^{EEM}}{\partial q_A} = \chi_A^* + q_A \eta_A^* + \sum_{B \neq A} \frac{q_B}{R_{AB}} = \alpha, \quad A = 1, \ldots, M. \tag{12}$$

Here, α is the Lagrange multiplier associated with the constraint, and it can be shown that it is equal to the molecular electronegativity:

$$\alpha = \frac{\partial E^{EEM}}{\partial Q} = \chi_{mol}. \tag{13}$$

One can identify the derivative in Eq. (12) with the Politzer–Weinstein [8] definition of the electronegativity of an atom-in-a-molecule, and this equation corresponds to the electronegativity equalization condition. The principle of electronegativity equalization states[9, 10] that the molecular electronegativity, Eq. (13), equals the derivative of the energy with respect to the charge on an atom A and that for all atoms A [8]. The resulting expressions for EEM are usually written in a matrix form as

$$\begin{bmatrix} \eta_1^* & 1/R_{12} & \cdots & 1/R_{1M} & 1 \\ 1/R_{12} & \eta_2^* & \cdots & 1/R_{2M} & 1 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 1/R_{1M} & 1/R_{2M} & \cdots & \eta_M^* & 1 \\ 1 & 1 & \cdots & 1 & 0 \end{bmatrix} \begin{bmatrix} q_1 \\ q_2 \\ \vdots \\ q_M \\ -\chi_{mol} \end{bmatrix} = \begin{bmatrix} -\chi_1^* \\ -\chi_2^* \\ \vdots \\ -\chi_M^* \\ Q \end{bmatrix}. \tag{14}$$

The values of the quasi-atomic electronegativity and hardness are obtained from a fitting procedure involving a training set of molecules. This fitting is mostly done in a least squares sense by finding the parameters that minimize the quadratic error between the ab initio computed charges and the ones obtained using a set of systematically improved parameters; see, for example, Refs. [11–18]. In practice, such fitting is far from trivial. Moreover, the parameters significantly depend on the definition used to define an atom in the molecule. There also remains one degree of freedom, that is, one can freely choose one electronegativity parameter and only optimize the others with respect to this chosen value. Besides this trivial degree of freedom, it has been observed by Bultinck et al. [14] that other sources of ambiguity in the parameters remain. Verstraelen et al. [18] recently performed an in-depth analysis of the ambiguity in the parameters, revealing that no unique set of parameters can be obtained. Nevertheless, it has been shown that the parameters derived in such a way are useful to predict atomic charges and different other properties [19, 20] of high quality in molecules not used in the training set for the regression. Moreover, EEM is a key ingredient of many new developments in polarizable force fields and reactive force fields [21–24].

In this work, we follow a different path to EEM parametrization by directly using Eq. (10). Instead of going through the atomic charges, we present an algorithm for the direct calculation of the energy for a given set of atomic charges (populations) and examine how good a sum of quadratic quasi-atom energies is. The parameters are obtained from simple molecules, usually diatomic ones although examples are given also for larger molecules. Once the parameters are known, it is also possible to test their quality by applying them in Eq. (14) to compute atomic charges, which, in turn, are compared to the ab initio charges.

2 Model

The use of the orbital concept in the Hartree–Fock (HF) and Kohn–Sham (KS) methods leads to similar variational equations: a coupled set of eigenvalue equations with a hermitian operator (See for example [7, 25]). This system of integro-differential equations is transformed into a matrix problem when we use a basis set. In both methods, one has to solve a generalized eigenvalue equation:

$$\mathbf{FC} = \varepsilon \mathbf{SC}. \tag{15}$$

When atom-centered basis sets are used, a very simple procedure to assign the electrons among the atoms of the molecule comes from Mulliken's approach [26]. Within this method, the number of electrons assigned to the atom A is given by

$$n_A = \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} S_{\mu\nu}, \quad P_{\mu\nu} \equiv \sum_{i=1}^{N} C_{i\mu} C_{i\nu} \tag{16}$$

where the μ and ν indices are used for the basis functions, and the first sum is restricted to only those basis functions centered on atom A, P is the density matrix, and N is the number of electrons in the molecule.

Additional restrictions can be incorporated into the variational problem by making use of the Lagrange multiplier technique [27–31]. For example, if we want to fix the population in the atoms 1, 2, …, r, then for each atom A = 1,...,r the constraint takes the form:

$$\begin{aligned} 0 = n_A - N_A &= \sum_{\mu \in A} \sum_{\nu} P_{\mu\nu} S_{\mu\nu} - N_A, \\ &= \sum_{\mu\nu} \delta_{A,I_\mu} P_{\mu\nu} S_{\mu\nu} - N_A \end{aligned} \tag{17}$$

Here, N_A represents the desired population on atom A, and I_μ represents the atom where the basis function χ_μ is centered. Note that the Kronecker delta is not zero only when the basis function χ_μ is centered in atom A.

The variational solution of the constrained problem comes from minimizing, with respect to the coefficients, the following quantity:

$$\begin{aligned} L = E^{\mathrm{RHF}}\left(\{C_{i\mu}\}\right) &- \sum_{ij} \varepsilon_{ij} \left(\sum_{\mu\nu} C_{i\mu} S_{\mu\nu} C_{j\nu} - \delta_{ij} \right) \\ &- \sum_{A=1}^{r} \lambda_A \left(\sum_{\mu\nu} \delta_{A,I_\mu} P_{\mu\nu} S_{\mu\nu} - N_A \right). \end{aligned} \tag{18}$$

Here, E^{RHF} is the expectation value of the hamiltonian operator with a single-determinant wave function. The second term comes from the orthonormalization condition of the molecular orbitals, while the third one arises from each population restriction. The Euler–Lagrange equations from this problem lead to a matrix problem similar to Eq. (15):

$$\mathbf{F}'\mathbf{C} = \varepsilon'\mathbf{S}\mathbf{C}. \tag{19}$$

The modified Fock matrix, $\mathbf{F}'$, has the form:

$$\mathbf{F}' = \mathbf{F} - \sum_{A=1}^{r} \lambda_A \mathbf{G}^A, \quad G^A_{\mu\nu} \equiv \frac{1}{2}\left(\delta_{A,I_\mu} + \delta_{A,I_\nu}\right) S_{\mu\nu}. \tag{20}$$

Note that the modified Fock matrix is also hermitian.

It is important to note that the eigenvalues from Eq. (19) no longer approximate the ionization energies. However, following Koopmans' idea, we find that the ionization energies can be estimated from

$$IP_k \approx -\varepsilon'_k - \sum_{A=1}^{r} \lambda_A n_{Ak} \tag{21}$$

where n_{Ak} represents the contribution of the k-th orbital to the Mulliken population of the atom A and is given by:

$$n_{Ak} \equiv \sum_{\mu \in A} \sum_{\nu} C_{k\mu} C_{k\nu} S_{\mu\nu}, \quad n_A = \sum_{k=1}^{N} n_{Ak}. \tag{22}$$

For a given set of values of the Lagrange multipliers, $\{\lambda_A\}$, one can solve Eq. (19) and obtain the corresponding energy, the set of the molecular orbital coefficients, and the population on each atom. Since the atomic populations depend on the values of the Lagrange multipliers, one can specify the desired atomic populations and then get the right values of the Lagrange multiplier by solving the constraints,

$$n_A(\{\lambda_B\}) - N_A = 0, \quad A, B = 1, \ldots, r. \tag{23}$$

This set of equations is solved by using a multidimensional Newton–Raphson, or quasi-Newton variant, in a few iterations within any degree of precision. Usually, we take$0 = \lambda_1^{(0)} = \lambda_2^{(0)} = \cdots$ as a starting guess point and displacements below 0.1 to estimate the gradients.

This procedure is implemented in a proof of principle RHF code, and all the results in this paper are computed with the minimal basis set STO-3G.

3 Results and discussion

First, we apply the constrained minimization procedure to diatomic molecules, both homo- and heteronuclear. In this case, there is only one constraint, since the total number of electrons in the molecule is fixed. In every test, we find that the energy shows a quadratic-like dependence on the charge of the atom with the constrained population. The minimum value always corresponds to the Hartree–Fock energy ($\lambda_1 = 0$) because the HF determinant minimizes the expectation value of the Hamiltonian operator. Table 1 shows the energy (E) and charge (q_1) of the first atom for different values of the Lagrange multiplier (λ_1) in some diatomic molecules. The dependence of the energy with the charge can be observed in Fig. 1 for two representative diatomic molecules. It is important to mention that some diatomic charged species (NO^+, O_2^{2+}, HO^-, CN^-) are also included in the test set and their behavior shows no difference with respect to the neutral molecules.

Polyatomic highly symmetric molecules involving only two nonequivalent atoms, such as H_2O, CO_2, CH_4, and CF_4, show the same behavior when one restricts the charge of one atom, see Fig. 2. For other molecules, one can restrict the population on all atoms, but one. It is even possible to fix the population on one or more molecular fragments. The results always show that the energy has a quadratic-like dependence with respect to the fixed charges. It is precisely the quality of this quadratic dependence that underlies EEM. Note that this behavior was previously also observed by Cioslowski et al. [31].

The quadratic-like behavior obtained with the constrained HF method can be used to obtain useful EEM parameters by making use of the quadratic fitting of E^{RHF} as a function of q. For example, for a diatomic molecule, with charge Q, Eq. (10) can be written in the following way:

$$E_{mol} = E_1^{o*} + E_2^{o*} + \chi_2^* Q + \frac{1}{2}\eta_2^* Q^2 + q_1\left(\chi_1^* - \chi_2^* - \eta_2^* Q + \frac{Q}{R}\right) + q_1^2\left(\frac{\eta_1^* + \eta_2^*}{2} - \frac{1}{R}\right). \tag{24}$$

For a neutral homonuclear molecule, the linear term vanishes and the hardness comes from the quadratic coefficient of the fitting; see, for example, Fig. 1. In contrast, relative electronegativities can be obtained from the linear coefficient of the fitting of the data from the heteronuclear molecules. EEM parameters of some atoms obtained by this procedure are found in Table 2.

The atomic charges and the molecular electronegativity are solved from Eq. (14). Table 3 shows the comparison between the Mulliken charges from a RHF calculation and those from the EEM, using the parameters from Table 2. One can see that the atomic charges from both methods are in fairly good agreement given that they were obtained from only few molecules. In the more traditional EEM approach, parameters are obtained from molecules that mostly contain atoms of (nearly) all elements considered. In the present case, on the other hand, for the hardness only homonuclear diatomics are used.

For larger molecules, we find that the energy of the constrained HF procedure also shows a quadratic dependence with respect to the atomic charges. It is important to remark that the quadratic behavior comes from a truncated Taylor expansion, Eq. (9), and for large charges it may fail. For those cases, there are two alternative options. In the

Table 1 Energy (in Hartree) and Mulliken's atomic charge of the first atom as a function of the Lagrange multiplier, for some diatomic molecules

λ	NN		CO		FF	
	q_N	E	q_C	E	q_F	E
−1.0	2.03	−106.525635	1.73	−110.530475	0.74	−195.651614
−0.9	1.85	−106.692935	1.62	−110.634766	0.69	−195.697961
−0.8	1.67	−106.849769	1.50	−110.737606	0.64	−195.745043
−0.7	1.48	−106.993748	1.37	−110.836596	0.57	−195.791558
−0.6	1.28	−107.122769	1.23	−110.929219	0.50	−195.836022
−0.5	1.07	−107.235017	1.08	−111.012983	0.43	−195.876883
−0.4	0.86	−107.328957	0.91	−111.085538	0.35	−195.912641
−0.3	0.65	−107.403332	0.75	−111.144760	0.27	−195.941953
−0.2	0.44	−107.457163	0.57	−111.188802	0.18	−195.963711
−0.1	0.22	−107.489744	0.39	−111.216114	0.09	−195.977100
0.0	0.00	−107.500651	0.20	−111.225446	0.00	−195.981619
0.1	−0.22	−107.489744	0.01	−111.215842	−0.09	−195.977100
0.2	−0.44	−107.457163	−0.19	−111.186619	−0.18	−195.963711
0.3	−0.65	−107.403332	−0.38	−111.137356	−0.27	−195.941953
0.4	−0.86	−107.328957	−0.58	−111.067872	−0.35	−195.912641
0.5	−1.07	−107.235017	−0.78	−110.978210	−0.43	−195.876883
0.6	−1.28	−107.122769	−0.98	−110.868621	−0.50	−195.836022
0.7	−1.48	−106.993748	−1.18	−110.739544	−0.57	−195.791558
0.8	−1.67	−106.849769	−1.38	−110.591599	−0.64	−195.745043
0.9	−1.85	−106.692935	−1.57	−110.425574	−0.69	−195.697961
1.0	−2.03	−106.525635	−1.77	−110.242423	−0.74	−195.651614

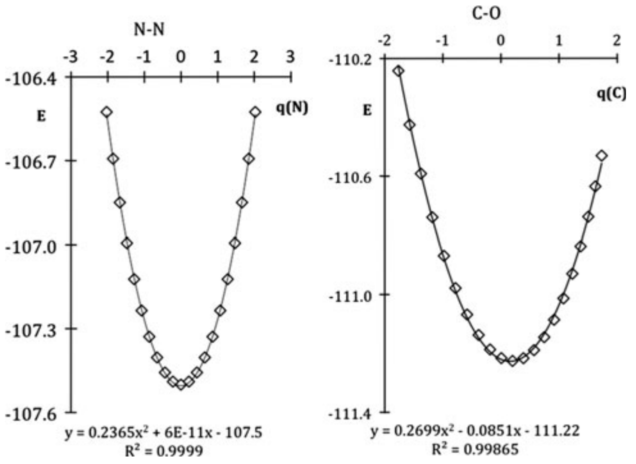

Fig. 1 Atomic charge–energy plots for two representative diatomic molecules. Energy values in Hartree. The *diamonds* are the results of the constrained RHF calculations, while the *curve* is a quadratic fit

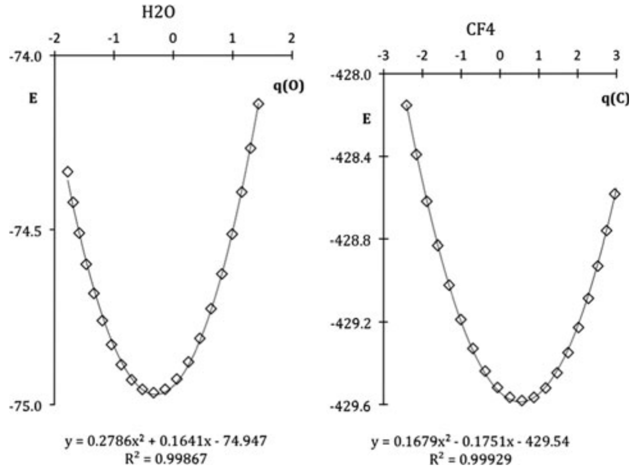

Fig. 2 Atomic charge–energy plots for two binary polyatomic molecules. Energy values in Hartree. The *diamonds* are the results of the constrained RHF calculations, while the *curve* is a quadratic fit

first option, one must add more terms to Eq. (9), which leads to a set of nonlinear equations, in addition to the need of new parameters. The second one consists in a shift of the reference system for the Taylor expansion, which keeps the quadratic form, but one has to take care of the terms from the shift and modify the equations accordingly. As a consequence, it is no longer possible to directly interpret relative values for EEM parameters (such as, e.g., the carbon versus oxygen electronegativity) with respect to expected trends in the periodic system as the latter are based on neutral atoms as reference.

To test whether the quadratic expansion applied to every atom still results in good regressions, some larger

Table 2 EEM parameters from the quadratic fitting of the constrained HF model

A	η_A^*	$\chi_A^* - \chi_H^*$
H	1.108	0.000
C	0.620	0.036
N	0.703	0.097
O	0.789	0.121
F	0.960	0.176

All values are reported in atomic units

The homonuclear diatomic molecules H_2, C_2, N_2, O_2^{2+}, and F_2 are used to obtain the quasi-atomic hardnesses, while CO, CN^-, OH^-, and HF are used for the quasi-atomic electronegativities. The procedure is described in the text

Table 3 EEM charges for some simple molecules computed with the parameters from Table 2

Molecule	Atom	Charge	
		EEM	HF
CO_2	C	0.36	0.44
	O	−0.18	−0.22
H_2O	H	0.14	0.17
	O	−0.27	−0.33
NH_3	N	−0.37	−0.44
	H	0.12	0.15
HCN	H	0.03	0.15
	C	0.11	0.01
	N	−0.14	−0.16
H_2CO	H	0.04	0.06
	C	0.07	0.07
	O	−0.15	−0.19
CH_4	C	−0.25	−0.26
	H	0.06	0.07
CF_4	C	0.53	0.57
	F	−0.13	−0.14

molecules were also included in the test set. As an example, we discuss the tetrahydrofurane molecule that contains 13 atoms. The straightforward adaptation of the algorithm developed above resulted in good performance although two further improvements were obtained upon changing two steps. The first is the use of a random assignment of atomic populations among all atoms but limited to within deviations from the reference of maximally 0.3 electrons for each atom. Second, the reference has been changed from neutral atoms to atoms with atomic population as found in the unconstrained Hartree–Fock minimum. Using as input a total of 130 (i.e., 10 times the number of atoms) constrained Hartree–Fock energy evaluations with randomly displaced atomic populations, parameters for the different atoms were fitted in a least square sense to minimize the difference between the constrained Hartree–Fock energy and that based on sums of quadratic atomic approximations. Using singular value decomposition to perform the least squares fit, we find that the summed quadratic model is very good with on average over the 130 points an absolute error in energy of ca. 0.5 milliHartree. Fig. 3 shows the regression quality between both data sets.

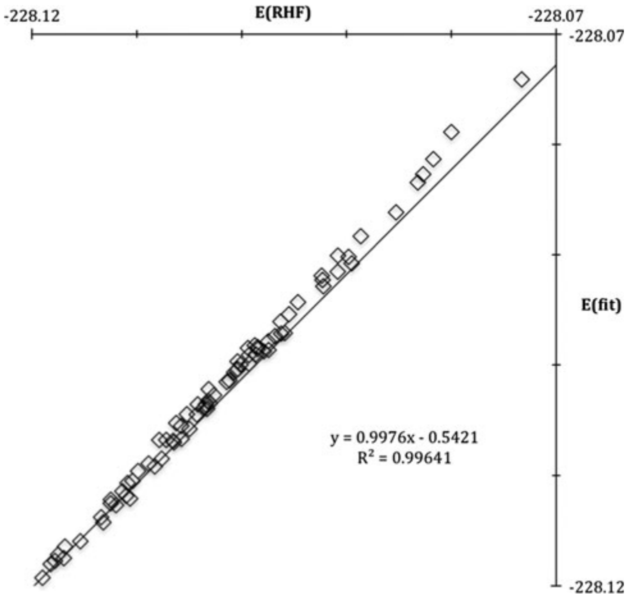

Fig. 3 Comparison between the constrained RHF energy and the quadratic fit for tetrahydrofurane. Energy values in Hartree

As a test of the performance of the optimized parameters in Mulliken charges derived from EEM expressions, we also compared both sets of charges, ab initio and EEM based. As expected on the basis of the excellent regression, the charges are also reproduced very well, see Table 4.

A remarkable feature of these results is that the quadratic form in Eq. (10) produces excellent fits to the constrained RHF data, even though the quadratic form is incomplete. The only off-diagonal quadratic terms are due to the electrostatic interaction between the atoms, Eq. (8).

For a different population analysis model, the constraint takes a different form. For example, in the Hirshfeld method [32], the atomic population takes the form:

$$n_A^H = \int w_A^H(\vec{r})\rho(\vec{r})\mathrm{d}\vec{r} = \sum_{\mu\nu} P_{\mu\nu} \int w_A^H(\vec{r})\chi_\mu(\vec{r})\chi_\nu(\vec{r})\mathrm{d}\vec{r} \equiv \sum_{\mu\nu} P_{\mu\nu} G_{\mu\nu}^A \tag{25}$$

where w_A^H are the Hirshfeld weight factors, which are independent of the molecular density. The constrained minimization leads to an Euler–Lagrange equation that has

Table 4 Comparison of the atomic charges from the fitting parameters and RHF for tetrahydrofurane

Atom	EEM	Mulliken
O	−0.275	−0.273
C_a	0.009	0.008
$C_{a'}$	0.007	0.008
C_b	−0.115	−0.117
$C_{b'}$	−0.117	−0.117
H_a	0.064	0.064
H_a	0.056	0.055
$H_{a'}$	0.065	0.064
$H_{a'}$	0.058	0.055
H_b	0.061	0.065
H_b	0.061	0.062
$H_{b'}$	0.064	0.065
$H_{b'}$	0.062	0.062

the same form of Eq. (19), but the modified Fock matrix becomes

$$F'_{\mu\nu} \equiv F_{\mu\nu} - \sum_A \lambda_A G^A_{\mu\nu}. \tag{26}$$

In other cases, a constraint written in terms of the coefficients or the density can be easily incorporated into the constrained procedure.

The implementation of our model in a KS code will be very similar to the procedure described above. A small variation in the parameters is expected due to the inclusion of the correlation effects, but not in the trend along the periodic table.

4 Concluding remarks

The addition of atomic charge constraints to the self-consistent RHF procedure yields a quadratic relationship between the energy and the atomic charges. This behavior provides an alternative way to obtain EEM parameters, which produce atomic charges in good agreement with those from the RHF method. The advantages of the present approach are that one can obtain EEM parameters from one specific molecule instead of requiring several sets of atomic charges for a range of molecules. Second, the performance of the constrained method numerically supports the assumptions from which the EEM is derived.

The use of other kinds of constraints in the electronic structure calculations is currently under exploration.

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References

1. Mortier WJ, Ghosh SK, Shankar S (1986) J Am Chem Soc 108:4315–4320
2. Mortier WJ (1987) In: Sen KD, Jorgensen CK (eds) Electronegativity. Springer, Berlin
3. Baekelandt BG, Mortier WJ, Schoonheydt RA (1992) In: Sen KD (ed) Chemical hardness. Springer, Berlin
4. Blanco MA, Martín-Pendás A, Francisco E (2005) J Chem Theory Comput 1:1096–1109
5. Vanfleteren D, Ghillemijn D, Van Neck D, Bultinck P, Waroquier M, Ayers PW (2011) J Comput Chem 32:3485–3496
6. Mayer I (2007) Faraday Discuss 135:439–450
7. Parr RG, Yang W (1989) Density functional theory of atoms and molecules. New York, Oxford
8. Politzer P, Weinstein H (1979) J Chem Phys 71:4218–4220
9. Sanderson RT (1951) Science 114:670
10. Sanderson RT (1983) Polar CoValence. Academic Press, New York
11. Baekelandt B, Mortier W, Lievens J, Schoonheydt R (1991) J Am Chem Soc 113:6730–6734
12. Rappe A, Goddard W (1991) J Phys Chem 95:3358–3363
13. Menegon G, Shimizu K, Farah JPS, Dias LG, Chaimovich H (2002) Phys Chem Chem Phys 4:5933–5936
14. Bultinck P, Langenaeker W, Lahorte P, De Proft F, Geerlings P, Waroquier M, Tollenaere JP (2002) J Phys Chem A 106:7887–7894
15. Bultinck P, Langenaeker W, Lahorte P, De Proft F, Geerlings P, Van Alsenoy C, Tollenaere JP (2002) J Phys Chem A 106:7895–7901
16. Bultinck P, Vanholme R, Popelier P, De Proft F, Geerlings P (2004) J Phys Chem A 108:10359–10366
17. Verstraelen T, Van Speybroeck V, Waroquier M (2009) J Chem Phys 131:044127
18. Verstraelen T, Bultinck P, Van Speybroeck V, Ayers PW, Van Neck D, Waroquier M (2011) J Chem Theory Comput 7:1750–1764
19. Bultinck P, Carbó-Dorca R (2002) Chem Phys Lett 364:357–362
20. Bultinck P, Langenaeker W, Carbó-Dorca R, Tollenaere JP (2003) J Chem Inf Comput Sci 43:422–428
21. York DM, Yang W (1996) J Chem Phys 104:159–172
22. Chelli R, Procacci P, Righini R, Califano S (1999) J Chem Phys 111:8569–8575
23. Warshel A, Kato M, Pisliakov AV (2007) J Chem Theory Comput 3:2034–2045
24. van Duin ACT, Strachan A, Stewman S, Zhang Q, Xu X, Goddard WA (2003) J Phys Chem A 107:3803–3811
25. Szabo A, Ostlund NS (1982) Modern quantum chemistry. Macmillan, New York
26. Mulliken RS (1955) J Chem Phys 23:1833–1840
27. Dederichs PH, Blügel S, Zeller R, Akai H (1984) Phys Rev Lett 53:2512–2515
28. Wu Q, Van Voorhis T (2005) Phys Rev A 72:024502
29. Wu Q, Van Voorhis T (2006) J Chem Theory Comput 2:765–774
30. Kaduk B, Kovalczyk T, Van Voorhis T (2012) Chem Rev 112:321–370
31. Cioslowski J, Stefanov BB (1993) J Chem Phys 99:5151–5162
32. Hirshfeld FL (1977) Theor Chim Acta 44:129–138