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Atomic Potentials from SCF Data

By

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The possibility is explored of representing atomic potentials, derived from SCF data, with function

$$V(R) = R^{-1} \sum_{i=1}^{\lambda} n_i \{\exp(-2\alpha_i R)\,[(2\alpha_i - V_i^0/n_i)\,R + 1] - 1\}$$

where n_i, α_i and V_i^0 are parameters. For two-electron systems, a general formula is derived. The results obtained for a limited number of many-electron systems and with only two terms in the fitting function indicate that it is likely that a general formula based on the abovementioned function will represent satisfactorily SCF atomic potentials for neutral atoms and ions.

On examine la possibilité de représenter des potentiels atomiques, dérivés de calculs SCF, par la fonction:

a) $$V(R) = R^{-1} \sum_{i=1}^{\lambda} n_i \{\exp(-2\alpha_i R)\,[(2\alpha_i - V_i^0/n_i)\,R + 1] - 1\}$$

où n_i, α_i et V_i^0 sont des paramètres.

Pour les systèmes diélectroniques est dérivée une formule commune. Les résultats obtenus pour un nombre limité de systèmes polyélectroniques (avec $\lambda = 2$) indiquent qu'une formule générale basée sur a) devrait représenter satisfaisamment les potentiels SCF pour les atomes neutres et ionisés.

Es wird die Möglichkeit untersucht, atomare Potentiale aus SCF Daten durch obige Funktion darzustellen. Für Zweielektronensysteme wird eine allgemeine Funktion abgeleitet. Die Ergebnisse, die man für eine Anzahl Mehr-Elektronensysteme (für $\lambda = 2$) erhält, lassen den obigen Ansatz für atomare Potentiale neutraler Atome und Ionen zufriedenstellend erscheinen.

In many perturbative problems, electrostatic approximations may often be sufficiently accurate to yield quantitative answers. This may be the case when dealing with non-specific interactions among molecules or ligand perturbation [2]. Examples of this situation may be found in electronic spectra of molecular crystals, molecular Rydberg series and possibly in generalized solvent effects in vibronic transitions or substituent perturbation on chemical shifts. In the latter cases other physical parameters may participate significantly, such as polarizabilities, magnetic anisotropies a.s.o.: even then, it seems desiderable to assess the weight of the electrostatic perturbation.

Since the latter is equivalent to a term in the hamiltonian operator and since the potential field generated by a molecule or a group, in an approximation which neglects exchange terms, may be built out of atomic potentials, it was thought worthwhile to obtain for the latter analytical functions as accurate as possible and at the same time simple enough to be handled with ease. For this purpose the possibility was explored of representing analytically potentials derived from self consistent field data for neutral atoms and ions.

Analytical function (1) was chosen: it is derived, by generalization, from the hydrogenlike 1s-electron potential:

$$V(R) = R^{-1} \overset{\lambda}{\underset{1}{\sum\nolimits_i}} n_i \{\exp(-2\,\alpha_i R)\,[(2\,\alpha_i - V_i^0/n_i)\,R + 1] - 1\} \tag{1}$$

where n_i, α_i and V_i^0 are parameters conditioned by (2a, b):

$$\overset{\lambda}{\underset{1}{\sum\nolimits_i}} n_i = n \tag{2a}$$

n being the number of electrons in the atomic system.

$$\overset{\lambda}{\underset{1}{\sum\nolimits_i}} V_i^0 = \overset{n}{\underset{1}{\sum\nolimits_i}} \langle R_i^{-1} \rangle \tag{2b}$$

$\langle R_i^{-1} \rangle$ being the reciprocal mean radius of the i-th electron.

Function (1) satisfies boundary conditions (3a, b):

$$\lim_{R \to \infty} [-RV(R)/n] = 1 \tag{3a}$$

$$\lim_{R \to 0} [-V(R)] = \overset{n}{\underset{1}{\sum\nolimits_i}} \int_0^\infty P_i^2(R)\,R^{-1}\,dR = \overset{n}{\underset{1}{\sum\nolimits_i}} \langle R_i^{-1} \rangle \tag{3b}$$

being $P_i(R)$ the i-th reduced radial self-consistent function.

Function (1) can be interpreted in two ways:

a) as a potential generated by reduced radial functions of type (4)

$$P_i(R) = 2\,\alpha_i\,n_i^{\frac{1}{2}}\,R\,[(\alpha_i + \beta_i) - \beta_i\,R^{-1}/\alpha_i]^{\frac{1}{2}} \exp(-\alpha_i R) \tag{4}$$

where $\beta_i = \alpha_i - V_i^0/n_i$[★].

Function (4) vanishes for $R = \beta_i/\alpha_i\,(\alpha_i + \beta_i)$ and at the boundaries, while it becomes imaginary when $R < \beta_i/\alpha_i\,(\alpha_i + \beta_i)$; the corresponding radial function $P_i(R)/R$ vanishes for $R \to \infty$ and approaches infinity when R goes to zero. These difficulties can be overcome by multiplying the negative term $\beta_i/R\alpha_i$ in eq. (4) by $[1 - f(R)]$, with $f(0) = 1$ and $f(R)$ becoming negligible for $R > \beta_i/\alpha_i\,(\alpha_i + \beta_i)$ and such as to keep positive the expression inside the square brackets. This will not modify appreciably neither the normalizing condition nor the mean radius. The former requires n_i to be unity while the latter is represented by V_i^0, which is fixed by boundary conditions [see eq. (2b, 3b)]. Thus (4) are essentially one parameter (α_i) functions: they do not form an orthonormal set since $P_i\,(n, l)$ is not orthogonal to $P_i\,(n', l)$: this can be cured by taking suitable linear combinations of (4), which corresponds to adding a term in eq. (1).

In this form eq. (1) may perhaps find some applications in aiding self-consistent field calculations of atomic systems or in molecular problems.

b) as a purely empirical function with n_i, α_i and V_i^0 fitting parameters subject to conditions (2a, b). Thus only $\overset{\lambda}{\underset{1}{\sum\nolimits_i}} n_i$ and $\overset{\lambda}{\underset{1}{\sum\nolimits_i}} V_i^0$ retain a physical significance.

In this exploratory investigation, interpretation b) was followed with some limitations hereafter specified: thus, being atomic charge distributions spherically

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[★] β_i can be taken as a measure of the deviation of the potential from the hydrogenlike form, since in the latter case it is zero.

symmetric, Poisson's equation was used to derive, from self-consistent field data, atomic potentials in numerical form. Double integration was performed with a method indicated by HARTREE [*3*] on the charge distributions of the following atomic systems (ground state except for carbon):

$$\text{He, Be}^{+}\text{, C}^{+4}\text{, Be, C}^{+2}\text{, B, O}^{+3}\text{, C } (sp^3)\text{, O}^{+2}\text{, N, O, F, Ne} \tag{5}$$

for which SCF functions are known in the literature [*3*, *5*].

When this investigation was already begun, STRAND and BOHNAM [*6*] published a paper dealing with analytical fittings of potentials derived from SCF data, with function (6) previously proposed by IBERS and HOERNI [*4*]:

$$Z(R)/Z = \sum_i {}^a\gamma_i \exp(-{}^a\lambda_i r) + \gamma \sum_j {}^b\gamma_j \exp(-{}^b\lambda_j r) \,. \tag{6}$$

Function (6) was applied only to neutral atoms.

c) *Two electron potentials.* For two-electron systems in the configuration $1s^2$ (He, Be^{+2}, C^{+4}), under the condition $\lambda = 1$*, eq. (1), inclusive of the nuclear term, becomes:

$$V(R) = R^{-1}\{2\,[(2\,\alpha_1 - V_1^0/2)\,R + 1]\exp(-2\,\alpha_1 R) + (Z-2)\} \tag{7}$$

Z being the nuclear charge.

This is a one-parameter (α_1) function since V_1^0 is fixed by boundary conditions. α_1 was optimized by minimizing integral (8):

$$\Delta U = \int_0^\delta |\, U(R) - U_n(R) \,|\, dR \tag{8}$$

where $U_n(R)$ is the numerical self-consistent field potential and δ a suitable value ($\sim$ 2 a. u. for the above cases).

Table 1

R.	He		Be^{+2}		C^{+4}	
a. u.	$U_n(R)$	eq. (10)	$U_n(R)$	eq. (10)	$U_n(R)$	eq. (10)
0.1	16.684	16.714	33.113	33.129	50.078	50.082
0.2	6.827	6.857	14.013	14.012	22.222	22.217
0.4	2.207	2.220	5.679	5.666	10.181	10.178
0.8	0.429	0.421	2.533	2.529	5.001	5.002
1.4	0.055	0.045	1.428	1.429	–	–

Linear correlations were found between α_1, V_1^0 and Z given by eq. (9a, b):

$$\alpha_1 = Z - 0.375 \qquad \Delta = 0.01 \tag{9a}$$

$$V_1^0/2 = Z - 0.302^{**} \qquad \Delta = 0.01 \tag{9b}$$

Δ = square mean deviations

which substituted in (7) lead to the extrapolated general expression (10) for two-

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* For $\lambda = 1$ interpretations a) and b) coincide so that one may represent the He-like $1s$-orbital with function (4) suitably corrected near the origin as previously indicated.

** Since $\langle R^{-1}\rangle$ for Slater's type orbitals is a function of the exponential factor, it can be seen that the screening constant for $1s$-electrons (0.30) derived from (9b) is exactly the usual Slater value.

electron ($1s^2$) potentials:

$$U(R) = R^{-1} \{2 [(Z - 0.448) R + 1] \exp [-2 (Z - 0.375) R] + (Z - 2)\} \quad (10)$$

which may be assumed to hold at least for first row elements. The deviation from hydrogenlike form is here not very large ($\beta = 0.073$). The accuracy of eq. (10) can be judged from the data collected in Tab. 1, where numerical SCF potentials $U_n(R)$ are compared with those derived from eq. (10) for a number of points.

d) *Many-electron potentials:* for the many-electron systems in (5), in order to limit the amount of computations, conditions (11) were imposed in eq. (1):

$$\lambda = 2 \quad (11\text{a})$$

$$\alpha_1 = Z - 0.375 \quad (11\text{b})$$

$$n_1 = 2 \,. \quad (11\text{c})$$

Function (1) contains now two fitting parameters α_2 and V_1^0 or V_2^0, since the sum of the latter is fixed by boundary conditions.

Optimization of the parameters was performed in a similar way to that followed in the two-electron case, by minimizing the deviations, not through integral (8), which would prove cumbersome with desk computing, but for a selected number of R-values in the range where the potential of each atomic system is more significant.

Table 2. *Parameters appearing in eq.* (1) ($\lambda = 2$, $n_1 = 2$, $\alpha_1 = Z - 0.375$) *for many-electron systems*

atomic system	α_2	V_1^0	V_2^0
Be	0.612	7.602	0.807
C^{+2}	1.280	12.262	1.163
B	0.753	9.799	1.438
O^{+3}	1.850	17.336	2.225
C (sp^3)	0.872	11.787	2.702
O^{+2}	1.730	17.758	2.968
N	1.207	14.285	4.305
O	1.609	17.760	3.850
F	1.367	17.330	8.796
Ne	1.578	19.842	10.951

In Tab. 2 are collected the optimum values of α_2 and V_1^0, V_2^0 for the many-electron systems listed in (5).

As expected from simple considerations on the reciprocal mean radius of Slater-type orbitals, a correlation exists between ($V_1^0 + V_2^0$) and Z, n expressed by eq. (12)*:

$$V_1^0 + V_2^0 = -0.138\, n^2 + 0.295\, nZ + 1.305\, Z + 0.231\, n - 0.266 \quad (12)$$

$$\Delta = 0.03 \,.$$

Although the number of atomic systems here investigated is limited, some regularities in the fitting parameters can still be observed (see for instance the case of O^{+3}, O^{+2}, O). Indeed for V_2^0 and α_2, a correlation exists with Z, n although at this stage may not be very significant.

The accuracy in representing potentials derived from SCF data for many-electron systems with the severe limitations (11) imposed, is usually lower than for the two-electron case, but still satisfactory.

From the present exploratory investigation it can be concluded that even with a limited number of parameters, function (1) represents with reasonable accuracy potentials derived from self-consistent field data and as such can be conveniently used in perturbative problems or to derive physical parameters of interest.

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* By using Slater's or Clementi's [*1*] set of screening parameters, one obtain equation for $\overset{n}{\underset{1}{\Sigma}}_i \langle R_i^{-1} \rangle$ similar to (12).

An improvement may be obtained by optimizing separately all parameters and perhaps by taking λ equal to the number of different atomic orbitals involved. In this case it is likely that a general formula similar to that obtained for two-electron systems can be derived, which applies to neutral atoms and ions.

References

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