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An Extension of the Least Squares Local Energy Method to Perturbed Systems

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The local energy method [1 – 8] has been used to obtain the zero order energies and wave functions of several simple systems. The method has the advantage that no integration is required, and, as used by Frost et al. [1, 3 – 7], it involves determining a wave function $\Psi^{(0)}$ by minimizing the variance of the quantity $\mathscr{H}^{(0)} \Psi^{(0)}/\Psi^{(0)}$ where $\mathscr{H}^{(0)}$ is the Hamiltonian for the system. Frost et al. have obtained good values for the zero order energies of He, H_2^+, H_2 and Li [4, 6, 7].

The method has obvious attractions for properties other than the zero order energy of molecules. Other molecular properties weight the wave function on a different way from $\mathscr{H}^{(0)}$, and the variance minimization technique can be used to ensure that the wave function is satisfactory in the most important part of the space. Thus, for calculations of field gradients at nuclei, the variance of $\mathscr{H}^{(0)} \Psi^{(0)}/\Psi^{(0)}$ can be minimized for points close to the nuclei, and for calculations of quadrupole and higher moments, the variance can be minimized for points distant from the nuclei. Properties depending on the first order energy can be calculated with a $\Psi^{(0)}$ obtained or improved in this way in accordance with the usual integral perturbation theory formula for the first order energy,

$$W^{(1)} = (\Psi^{(0)} \,|\, \mathscr{H}^{(1)} \,|\, \Psi^{(0)}) \,, \tag{1}$$

where $\mathscr{H}^{(1)}$ is the Hamiltonian corresponding to the perturbation. With this procedure the least squares local energy method would be an adjunct to the usual non-empirical calculation by the variation method.

The integration in Eq. (1) can, however, be avoided if the higher order perturbation equations are solved, and the object of this note is to show how the least squares local energy method can be extended to obtain higher order energies, and thus to a wide range of molecular properties.

The first order perturbation equation may be written [9],

$$[\mathscr{H}^{(0)} - W^{(0)}] \, \Psi^{(1)}/\Psi^{(0)} + \mathscr{H}^{(1)} \, \Psi^{(0)}/\Psi^{(0)} = W^{(1)} \,, \tag{2}$$

and this can be solved by obtaining a $\Psi^{(1)}$ that minimizes the variance of $W^{(1)}$ for a series of points. Eq. (2) is the basis of a least squares local energy method for the first order perturbed wave function and energy. The method can clearly be extended to higher orders, thus $W^{(2)}$ can be obtained by minimizing the variance in the equation,

$$[\mathscr{H}^{(0)} - W^{(0)}] \, \Psi^{(2)}/\Psi^{(0)} + [\mathscr{H}^{(1)} - W^{(1)}] \, \Psi^{(1)}/\Psi^{(0)} + \mathscr{H}^{(2)} \, \Psi^{(0)}/\Psi^{(0)} = W^{(2)} \,, \tag{3}$$

a form that would apply to calculations of the diamagnetic susceptibility and nuclear shielding [9]. The first object of this work is, however, to find a practicable method of obtaining $\Psi^{(1)}$ and $W^{(1)}$ from Eq. (2). The notation used is similar to that of FROST, KELLOGG, GIMARC, and SCARGLE [4].

Let the value of the quantities in Eq. (2) evaluated at a point P be denoted by a subscript P, then it may be written,

$$\varepsilon_P^{(1)} = [\mathscr{H}_P^{(0)} - \varepsilon_P^{(0)}]\, \Psi_P^{(1)}/\Psi_P^{(0)} + \mathscr{H}_P^{(1)}\, \Psi_P^{(0)}/\Psi_P^{(0)} . \tag{4}$$

$\varepsilon_P^{(0)}$ and $\Psi_P^{(0)}$ are obtained in a zero order calculation. $\Psi^{(1)}$ may be written,

$$\Psi^{(1)} = \sum_r c_r^{(1)}\, \phi_r , \qquad r = 1, 2 \ldots N , \tag{5}$$

and the variance $V^{(1)}$ is given by,

$$V^{(1)} = \langle \varepsilon^{(1)2} \rangle - \langle \varepsilon^{(1)} \rangle^2 , \tag{6}$$

where

$$\langle \varepsilon^{(1)} \rangle = \sum_P g_P^{(1)}\, \varepsilon_P^{(1)} / \sum_P g_P^{(1)} , \tag{7}$$

$$\langle \varepsilon^{(1)2} \rangle = \sum_P g_P^{(1)}\, \varepsilon_P^{(1)2} / \sum_P g_P^{(1)} , \tag{8}$$

the $g_P^{(1)}$ being weight factors for the points P. As suggested by FROST et al. $g_P^{(1)}$ may be written,

$$g_P^{(1)} = w_P\, \Psi_P^{(0)2} , \tag{9}$$

or

$$g_P^{(1)} = w_P\, \Psi_P^{(1)2} , \tag{10}$$

where the w_P are input data. FROST et al. [4] have suggested that the best choice of P and w_P is as in Gaussian quadrature; but this choice is not appropriate for the higher order energies, where the type of perturbation must determine the points and weights, in accordance with the principle stated above.

The $c_r^{(1)}$ are determined from the equations,

$$\partial V^{(1)} / \partial c_r^{(1)} = 0 , \tag{11}$$

and from (4) – (10) it follows by some tedious algebra that (11) may be written,

$$\begin{aligned} 2 \sum_P g_P^{(1)}\, \varepsilon_P^{(1)}\, \partial \varepsilon_P^{(1)} / \partial c_t^{(1)} + \sum_P \varepsilon_P^{(1)}\, \partial g_P^{(1)2} / \partial c_t^{(1)} - 2 \langle \varepsilon^{(1)} \rangle \sum_P [g_P^{(1)}\, \partial \varepsilon_P^{(1)} / \partial c_t^{(1)} + \varepsilon_P^{(1)}\, \partial g_P^{(1)} / \partial c_t^{(1)}] \\ + \sum_P c_r^{(1)} [\langle \varepsilon^{(1)} \rangle^2 - V^{(1)}]\, S_{rt} = 0 , \qquad t = 1, 2 \ldots N , \end{aligned} \tag{12}$$

where

$$S_{rt} = \sum_P w_P\, \phi_r(P)\, \phi_t(P) , \tag{13}$$

$\phi_r(P)$, $\phi_t(P)$ being the functions ϕ_r, ϕ_t evaluated at the point P.

If $\partial g_P^{(1)} / \partial c_P^{(1)} = 0$, following the definition given in (9), then (12) becomes

$$\sum_P g_r^{(1)}\, \varepsilon_P^{(1)}\, \partial \varepsilon_P^{(1)} / \partial c_t^{(1)} - \langle \varepsilon^{(1)} \rangle \sum_P g_P^{(1)}\, \partial \varepsilon_P^{(1)} / \partial c_t^{(1)} = 0 \tag{14}$$

and from (4), (14) becomes,

$$\sum_r c_r^{(1)}\, [G'_{rt} - H'_{rt} - L'_{rt} + S'_{rt}] + H_t - M_t = 0 \tag{15}$$

where,

$$S'_{rt} = \sum_P w_P\, \varepsilon_P^{(0)2}\, \phi_r(P)\, \phi_t(P)$$

$$G'_{rt} = \sum_P w_P \mathcal{H}_P^{(0)} \phi_r(P) \mathcal{H}_P^{(0)} \phi_t(P)$$

$$H'_{rt} = \sum_P w_P \varepsilon_P^{(0)} \{[\mathcal{H}_P^{(0)} \phi_r(P)] \phi_t(P) + \phi_r(P) \mathcal{H}_P^{(0)} \phi_t(P)\}$$

$$L'_{rt} = \sum_P A_r A_t / \sum_P g_P \,, \tag{16}$$

where

$$A_r = \sum_P w_P \Psi_P^{(0)} [\mathcal{H}^{(0)} - \varepsilon_P^{(0)}] \phi_r(P) \,,$$

$$M_t = \sum_P w_P \Psi_P^{(0)} \mathcal{H}^{(1)} \Psi_P^{(0)} A_t / \sum_P g_P$$

$$H_t = \sum_P w_P \mathcal{H}^{(1)} \Psi_P^{(0)} [\mathcal{H}^{(0)} - \varepsilon_P^{(0)}] \phi_t(P) \,.$$

The determination of the $c_r^{(1)}$ and thus of $W^{(1)}$, which may be equated to $\langle \varepsilon^{(1)} \rangle$, involves the solution of the inhomogeneous simultaneous equations given by (15).

The most important decisions involve the choice of basis functions ϕ_r and the points P. The only complicated algebra comes from the term $\mathcal{H}^{(0)} \Psi^{(1)}$ in Eq. (4). The second and higher order equations may be obtained similarly.

An obvious model system on which to test the method is the hydrogen molecule. Harriss and Frost [7] have described a least squares local energy calculation of $W^{(0)}$ and $\Psi^{(0)}$ for this molecule involving a James-Coolidge type wave function with spheroidal basis functions, ξ, η, thus,

$$\Psi^{(0)} = \sum_{k,\,l,\,m,\,n,\,p} e^{-\alpha(\xi_1+\xi_2)} \xi_1^k \xi_2^l \eta_1^m \eta_2^n r_{12}^p c_{klmnp}^{(0)} \,. \tag{17}$$

The programme used by them was the starting point for the work reported here. If $\Psi^{(1)}$ is written as in (17) with $c_{klmnp}^{(1)}$ replacing $c_{klmnp}^{(0)}$, $\mathcal{H}^{(0)} \Psi^{(1)}$ can clearly be evaluated in the same way as $\mathcal{H}^{(0)} \Psi^{(0)}$. The rest of the programme then simply involves setting up Eq. (15), and solving for $c_{klmnp}^{(1)}$ with a library sub-routine. The programme was written in Fortran II for the N.I.R.N.S. Atlas computer at Chilton, and it was arranged so that $\mathcal{H}^{(1)}$ forms a separate Fortran function which can be changed at will.

Preliminary calculations have been made for the field gradient and quadrupole moment of the hydrogen molecule, and the results will be presented later.

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