Schrödinger local energies

Serafin Fraga
Division of Theoretical Chemistry, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2
(Received 24 April 1978; revised manuscript received 14 June 1978)

Some local characteristics of the Schrödinger equation for two-electron atomic systems, as a functional, are investigated from a mathematical point of view and the possibility of their application to the semiempirical determination of energy levels is examined.

DEFINITIONS

The Schrödinger equation for the ith state of a two-electron atomic system, with nuclear charge Z, may be written (in atomic units and using standard notation) as

$$(T - Z/r_1 - Z/r_2 + 1/r_{12})\Psi_i = \Psi_i E_i\,, \tag{1}$$

where T denotes the total electronic kinetic energy operator. The electronic configuration space is defined by six variables, three per electron, but for the discussion in this work it is sufficient to consider the three variables, r_1, r_2, and r_{12}: that is, all those points with the same values of r_1, r_2, and r_{12} (although differing in the remaining variables) will be considered to define the same configuration point.

Equation (1) may be rewritten as

$$T\Psi_i = [E_i + Z/r_1 + Z/r_2 - 1/r_{12}]\Psi_i\,. \tag{2}$$

or

$$(T - E_i)\Psi_i = [Z/r_1 + Z/r_2 - 1/r_{12}]\Psi_i\,, \tag{3}$$

where the values of $T\Psi_i$ and $(T - E_i)\Psi_i$, at a given point $(r_1, r_2, r_{12})_k$, represent the local kinetic and potential energies, respectively.

Inspection of Eq. (2) shows that, given an eigenfunction Ψ_i with corresponding eigenvalue $E_i < 0$, there exists, in addition to or including those points of the configuration space where Ψ_i may vanish identically, a region where the local kinetic energy vanishes. Two eigenfunctions, Ψ_i and Ψ_j, with corresponding eigenvalues, $E_i < 0, E_j < 0, E_i \neq E_j$, do not have the same null local kinetic energy regions, unless Ψ_i vanishes identically at all the points of the region of null local kinetic energy associated with Ψ_j and/or Ψ_j vanishes identically at all the points of the region of null local kinetic energy associated with Ψ_i.

A region of null local potential energy may be defined, in a similar fashion, from Eq. (3). The difference, however, is that such a region is common to all the eigenstates of the Schrödinger equation and for that reason the discussion will be centered on the null local kinetic energy regions, hereafter abbreviated as NLKE regions.

Recasting the condition for a NLKE region as

$$E_i = 1/r_{12} - Z/r_1 - Z/r_2$$
$$= [r_1 r_2 - Z r_{12}(r_1 + r_2)]/r_1 r_2 r_{12}$$

and writing

$$r_2 = r_1 + \Delta r\,, \quad \Delta r \geqslant 0$$
$$\Delta r \leqslant r_{12} \leqslant 2r_1 + \Delta r\,,$$

one obtains

$$E_i = \frac{[r_1(r_1 + \Delta r) - Z(2r_1 + \Delta r)\Delta r]}{r_1(r_1 + \Delta r)\Delta r}$$

$$E_i = \frac{[r_1(r_1 + \Delta r) - Z(2r_1 + \Delta r)^2]}{r_1(r_1 + \Delta r)(2r_1 + \Delta r)}$$

for the two limiting values of r_{12}, respectively. (An equivalent formulation may be given, of course, for the case $r_1 = r_2 + \Delta r$.) The limiting values are then (a) $r_{12} = \Delta r$: $E_i \to \infty$ when $\Delta r \to 0$ and $E_i \to -Z/r_1$ when $\Delta r \to \infty$; (b) $r_{12} = 2r_1 + \Delta r$: $E_i \to (1 - 4Z)/2r_1$ when $\Delta r \to 0$ and $E_i \to -Z/r_1$ when $\Delta r \to \infty$. The two equations

$$r_{li} = -Z/E_i$$
$$r_{ui} = (1 - 4Z)/2E_i$$

may be used to characterize a NLKE region.

For any two eigenvalues, E_i and E_j, the above definitions allow us to write

$$-Z = r_{li}E_i = r_{lj}E_j\,,$$
$$(1 - 4Z)/2 = r_{ui}E_i = r_{uj}E_j\,.$$

POSSIBLE APPLICATIONS

The energy levels, referred to the ground state, may be expressed in terms of the corresponding values of r_l and/or r_u. For example, one such expression is

$$\Delta E_n = E_n - E_0 = -Z/r_{ln} - (1 - 4Z)/2r_{u0}\,,$$

which can be rewritten as

$$\Delta E_n = (Z/r_{u0})\{(4Z - 1)/2Z - 1/(1 + s_n)\}$$

TABLE I. Values of K_n for some states of the two-electron isoelectronic series.[a]

Configuration state	$1s2s$ $^3S_1$		$1s2p$ $^3P_2$		$1s2p$ $^1P_1$	
Z	K	ΔK	K	ΔK	K	ΔK
2	106 567		112 721		114 086	
		83 852		84 989		86 640
3	190 418		197 709		200 726	
		82 866		83 252		84 264
4	273 285		280 961		284 990	
		82 606		82 802		83 459
5	355 890		363 763		368 449	
		82 522		82 653		83 049
6	438 412		446 416		451 498	
		82 424		82 595		82 932
7	520 907		529 011		534 430	
		82 472		82 560		82 797
8	603 379		611 571		617 227	
		82 495		82 578		82 762
9	685 873		694 149		699 989	

[a] Experimental values used in the calculations have been taken from C. E. Moore, *Atomic Energy Levels*. Natl. Bur. Stand. Circular No. 467 (U.S. GPO, Washington, D. C., 1949).

with $s_n = (r_{1n} - r_{u0})/r_{u0}$.

This equation may be approximated, for s_n small small, by

$$\Delta E_n = K_n Z[(4Z - 1)/2Z - 1]$$

where K_n stands for $1/r_{u0}$.

The possible interest of this expression lies in the fact, as observed in Table I, that K_n presents an almost linear dependence on Z. (In this connection it must be remembered that the experimental data include contributions from interactions not present in the Schrödinger equation.) For brevity, only three states have been included in Table I, but the same kind of behavior is observed for other states, for which sufficient data are available.