

## Zero potential energy criterion for approximate wave functions

|       |  |
|-------|--|
| メタデータ | <p>言語: English</p> <p>出版者: American Institute of Physics</p> <p>公開日: 2012-03-16</p> <p>キーワード (Ja):</p> <p>キーワード (En): WAVE FUNCTIONS, POTENTIAL ENERGY, HYDROGEN IONS 1 PLUS, MOLECULAR IONS, ELECTRONIC STRUCTURE</p> <p>作成者: 古賀, 俊勝</p> <p>メールアドレス:</p> <p>所属:</p> |
| URL   | <a href="http://hdl.handle.net/10258/935">http://hdl.handle.net/10258/935</a>  |

# Zero potential energy criterion for approximate wave functions

Toshikatsu Koga

Department of Applied Chemistry and Department of Applied Science for Energy, Muroran Institute of Technology, Muroran, Hokkaido 050, Japan

(Received 3 July 1985; accepted 4 September 1985)

A zero potential energy expression, which is a possible partner to the zero momentum energy expression presented previously, is proposed and discussed as a criterion for assessing the accuracy of approximate wave functions. Applicability of these criteria is illustrated and compared for several approximate wave functions for the  $1s\sigma_g$  and  $2p\sigma_u$  states of the  $H_2^+$  molecule.

As a sensitive criterion for assessing the accuracy of approximate wave functions, Armstrong<sup>1</sup> and Thakkar and Smith<sup>2</sup> proposed and examined the zero momentum energy expression. The expression was derived by considering the local energy formula in momentum space instead of the ordinary one in position space,<sup>3</sup> and by taking the local energy at one particular point, i.e., the origin of coordinates in momentum space where the electron momenta vanish. Since zero momenta directly imply zero kinetic energy, the zero momentum energy formula is a special form of the local energy formula with vanishing kinetic energy contribution. Then there will be a counterpart special form of the local energy formula with vanishing potential energy contribution—which is investigated in this study.

The  $N$ -electron Schrödinger equations in position and momentum spaces are written in their local energy forms as

$$E = \left[ \sum_{i=1}^N (-\frac{1}{2}\Delta_i) \Psi(\mathbf{r}) \right] / \Psi(\mathbf{r}) + V(\mathbf{r}), \quad (1a)$$

$$E = \sum_{i=1}^N (1/2|\mathbf{p}_i|^2) + \left[ \int d\mathbf{p}' W(\mathbf{p} - \mathbf{p}') \Phi(\mathbf{p}') \right] / \Phi(\mathbf{p}), \quad (1b)$$

where  $\mathbf{r} = (\mathbf{r}_i)$  and  $\mathbf{p} = (\mathbf{p}_i)$  are position and momentum vectors of the electrons, respectively. (Atomic units are used throughout this paper.) The wave functions  $\Psi(\mathbf{r})$  and  $\Phi(\mathbf{p})$  and the potential energy operators  $V(\mathbf{r})$  and  $W(\mathbf{p})$  in the position and momentum representations are related through the Fourier transformation

$$\Phi(\mathbf{p}) = (2\pi)^{-3N/2} \int d\mathbf{r} \Psi(\mathbf{r}) \exp(-i\mathbf{r} \cdot \mathbf{p}), \quad (2a)$$

$$\Psi(\mathbf{r}) = (2\pi)^{-3N/2} \int d\mathbf{p} \Phi(\mathbf{p}) \exp(+i\mathbf{r} \cdot \mathbf{p}), \quad (2b)$$

$$W(\mathbf{p}) = (2\pi)^{-3N} \int d\mathbf{r} V(\mathbf{r}) \exp(-i\mathbf{r} \cdot \mathbf{p}), \quad (3a)$$

$$V(\mathbf{r}) = \int d\mathbf{p} W(\mathbf{p}) \exp(+i\mathbf{r} \cdot \mathbf{p}), \quad (3b)$$

where  $\mathbf{r} \cdot \mathbf{p}$  means  $\sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{p}_i$ .

If we set  $\mathbf{p} = (\mathbf{p}_i) = (0)$  in Eq. (1b), the kinetic energy part vanishes and we have the zero momentum (zm) energy expression<sup>2</sup>

$$E_{zm} = \left[ \int d\mathbf{p}' W(-\mathbf{p}') \Phi(\mathbf{p}') \right] / \Phi(0) \quad (4a)$$

$$= \left[ \int d\mathbf{r} V(\mathbf{r}) \Psi(\mathbf{r}) \right] / \left[ \int d\mathbf{r} \Psi(\mathbf{r}) \right]. \quad (4b)$$

Equation (4b) can be obtained by substituting the relations (2a) and (3a) into Eq. (4a).

A corresponding expression with zero potential (zp) energy contribution may be obtained from Eq. (1a) as

$$E_{zp} = \lim_{V \rightarrow 0} \left[ \sum_{i=1}^N (-1/2\Delta_i) \Psi(\mathbf{r}) \right] / \Psi(\mathbf{r}) \quad (5a)$$

$$= \lim_{V \rightarrow 0} \left[ \sum_{i=1}^N \int d\mathbf{p} (1/2|\mathbf{p}_i|^2) \Phi(\mathbf{p}) \exp(+i\mathbf{r} \cdot \mathbf{p}) \right] / \left[ \int d\mathbf{p} \Phi(\mathbf{p}) \exp(+i\mathbf{r} \cdot \mathbf{p}) \right], \quad (5b)$$

where  $\lim_{V \rightarrow 0}$  means that  $(\mathbf{r}_i)$  are so varied that the potential energy  $V(\mathbf{r})$  approaches zero. Equation (5b) can be derived from Eq. (5a) by using the relation (2b). Differently from  $E_{zm}$ , the expression for  $E_{zp}$  depends on the explicit form of  $V(\mathbf{r})$ . When  $V \rightarrow 0$  results from  $\mathbf{r} \rightarrow 0$  (e.g., harmonic oscillator), Eq. (5b) takes a simple form,

$$E_{zp} = \left[ \sum_{i=1}^N \int d\mathbf{p} (1/2|\mathbf{p}_i|^2) \Phi(\mathbf{p}) \right] / \left[ \int d\mathbf{p} \Phi(\mathbf{p}) \right], \quad (5c)$$

which is very similar to Eq. (4b). However, for atoms and molecules of our interest, we must consider a point infinitely apart from the nuclei where Coulombic interactions disappear. Therefore,  $E_{zp}$  measures the quality of wave functions at their long-range tails. [In this case, we omit the nuclear repulsion term from  $V(\mathbf{r})$  and  $E_{zp}$  represents the electronic energy for the sake of simplicity.]

Now we assume that  $\Psi(\mathbf{r})$  and  $\Phi(\mathbf{p})$  are normalized approximate wave functions and define the average (av) energy  $E_{av}$  by

$$E_{av} = \int d\mathbf{r} \Psi^*(\mathbf{r}) \left[ \sum_{i=1}^N (-\frac{1}{2}\Delta_i) + V(\mathbf{r}) \right] \Psi(\mathbf{r}) \quad (6a)$$

$$= \int d\mathbf{p} \Phi^*(\mathbf{p}) \left[ \sum_{i=1}^N (1/2|\mathbf{p}_i|^2) \Phi(\mathbf{p}) + \int d\mathbf{p}' W(\mathbf{p} - \mathbf{p}') \Phi(\mathbf{p}') \right]. \quad (6b)$$

By the variational principle,  $E_{av}$  is then an upper bound to the true energy  $E$ . On the other hand,  $E_{zm}$  is not bounded and  $E_{zm} = E$  is a necessary but not sufficient condition for the "approximate" wave function to be the true wave function.<sup>2</sup> The same discussion holds for the present zero potential energy expression  $E_{zp}$ . From Eqs. (4b) and (5a), however, we have the following differences between the criteria  $E_{zp}$  and  $E_{zm}$ :

(1)  $E_{zp}$  is easier to calculate than  $E_{zm}$ , since the former includes only differentiations.

(2) However, the limiting process  $V \rightarrow 0$  needs human analysis for each different type of wave function. Moreover,  $E_{zp}$  may not always exist; for example,  $E_{zp}$  for the single  $1s$  Gaussian approximation to the ground-state hydrogen atom is divergent.

(3) The criterion  $E_{zm}$  applies only to spatially totally symmetric singlet states,<sup>2</sup> because otherwise both of the denominator and numerator in Eqs. (4a) and (4b) vanish. On the other hand,  $E_{zp}$  does not suffer such restriction.

(4) Some parallelism between  $E_{zp}$  and  $E_{zm}$  is expected for atoms and molecules. For the Coulombic interaction, it is clear from Eq. (5a) that a diffuse component of  $\Psi(\mathbf{r})$  gives a major contribution to  $E_{zp}$ . At the same time, this diffuse component will be dominant in the vicinity of the origin in momentum space, since the position and momentum representations emphasize inverse regions of the respective spaces.

As an illustration, we have calculated the three energies  $E_{av}$ ,  $E_{zm}$ , and  $E_{zp}$  for the  $1s\sigma_g$  and  $2p\sigma_u$  states of the  $H_2^+$  molecule ion. Because of its prototypical bonding and antibonding characters, several approximate wave functions with different levels of accuracy are known for this molecule. The functions examined here are summarized in Table I. (The internuclear distance is fixed to 2 in all cases. Param-

eters are optimum values except for the Pauling and exact functions. For the explicit functional forms and the meaning of parameters, see references cited.)

The results are compared in Table II for the  $1s\sigma_g$  state and in Table III for the  $2p\sigma_u$  state. The entries of the tables are arranged in the order of improving variational energies. In the  $1s\sigma_g$  state, we see that  $E_{zm}$  is more sensitive than  $E_{av}$ , and  $E_{zp}$  is much more sensitive than  $E_{zm}$  to the accuracy of wave functions. In the crudest approximation of single  $1sAO$ , e.g.,  $E_{av}$  assigns 88% accuracy, but  $E_{zm}$  and  $E_{zp}$  assign, respectively, 75% and only 38% accuracies relative to the exact value. The expected parallelism between  $E_{zm}$  and  $E_{zp}$  is also clear. For the wave functions examined in Table II, not only  $E_{av}$  but also  $E_{zm}$  and  $E_{zp}$  are accidentally bounded by the exact energy, and all three of these criteria suggest almost the same order of accuracies of the wave functions. The inversion of the order of James and Guillemin-Zener functions is insignificant, but the inversion between Dickinson-a and Dickinson-b functions seems to be meaningful: According to the criteria  $E_{zm}$  and  $E_{zp}$ , the improvement of  $E_{av}$  by the double  $\zeta$  variation slightly deteriorates the long-range behavior of the wave functions. (For the correct long-range behavior of one-electron molecular wave functions, see Refs. 16 and 17.) The sensitive nature of  $E_{zp}$  is also found for the  $2p\sigma_u$  state to which  $E_{zm}$  is not applicable (Table III). In this case, however, the assessed orders of ac-

TABLE I. Summary of the  $H_2^+$  wave functions examined.

| Wave function                        | Parameters  |   |
|--------------------------------------|---|---|
|                                      | $1s\sigma_g$ state  | $2p\sigma_u$ state  |
| Single hydrogenic<br>AO at midpoint  | $1s$ with $\zeta = 0.911\ 76$   | $2p\sigma$ with $\zeta = 1.096\ 58$                         |
| Pauling (Ref. 4)                     | $\zeta = 1.0$   | $\zeta = 1.0$   |
| Finkelstein-Horowitz<br>(Ref. 5)     | $\zeta = 1.238\ 70$   | $\zeta = 0.900\ 45$   |
| Scaled floating<br>(Refs. 6 and 7)   | $\zeta = 1.242\ 30$<br>$x = 0.093\ 25$  | $\zeta = 0.906\ 55$<br>$x = -0.019\ 06$                     |
| Dickinson (Refs. 8-10)               | Case (a) $\begin{cases} \zeta_1 = \zeta_2 = 1.254\ 77 \\ c_2/c_1 = 0.160\ 53 \end{cases}$   | $\zeta_1 = \zeta_2 = 0.905\ 70$<br>$c_2/c_1 = -0.004\ 83$   |
|                                      | Case (b) $\begin{cases} \zeta_1 = 1.2459, \zeta_2 = 1.4826 \\ c_2/c_1 = 0.1379 \end{cases}$ | $\zeta_1 = 0.8356, \zeta_2 = 0.6325$<br>$c_2/c_1 = -0.0503$ |
| James (Refs. 11 and 12)              | $\delta = 1.353\ 95$<br>$c = 0.447\ 99$   | $\delta = 0.900\ 35$<br>$c' = 0.142\ 69$                    |
| Guillemin-Zener<br>(Refs. 13 and 14) | $a = 1.353\ 9$<br>$b = 0.919\ 1$  | $a = 0.900\ 3$<br>$b = 0.904\ 2$                            |
| Exact (Ref. 15)                      | ...   | ...   |

TABLE II. Zero momentum and zero potential energy tests of several wave functions for the  $1s\sigma_g$  state of  $H_2^+$ .

| Wave function        | $E_{av}$  | $E_{zm}$  | $E_{zp}$  |
|----------------------|-----------|-----------|-----------|
| Single $1s$          | -0.967 01 | -0.830 00 | -0.415 65 |
| Pauling              | -1.053 77 | -0.864 66 | -0.500 00 |
| Finkelstein-Horowitz | -1.086 51 | -1.025 37 | -0.767 19 |
| Scaled floating      | -1.094 15 | -1.037 07 | -0.771 65 |
| Dickinson-a          | -1.099 80 | -1.073 85 | -0.787 22 |
| Dickinson-b          | -1.100 36 | -1.058 74 | -0.776 13 |
| James                | -1.102 39 | -1.086 55 | -0.916 59 |
| Guillemin-Zener      | -1.102 44 | -1.086 56 | -0.916 52 |
| Exact                | -1.102 62 | -1.102 62 | -1.102 62 |

curacies are quite different and almost opposite depending on the criteria  $E_{av}$  and  $E_{zp}$ . Particularly,  $E_{zp}$  suggests the considerably wrong behavior of Dickinson-b function in its long-range region, so long as the parameters reported in the literature<sup>10</sup> are employed. In contrast to the  $1s\sigma_g$  state, where we can regard the James and Guillemin-Zener functions as fairly accomplished approximations, none of seven approximate wave functions simultaneously give satisfactory results for  $E_{av}$  and  $E_{zm}$  in the  $2p\sigma_u$  state.

TABLE III. Zero potential energy test of several wave functions for the  $2p\sigma_u$  state of  $H_2^+$ .

| Wave Function        | $E_{av}$  | $E_{zp}$  |
|----------------------|-----------|-----------|
| Single $2p\sigma$    | -0.604 14 | -0.601 24 |
| Pauling              | -0.660 85 | -0.500 00 |
| Guillemin-Zener      | -0.665 81 | -0.405 27 |
| James                | -0.665 81 | -0.405 32 |
| Finkelstein-Horowitz | -0.665 81 | -0.405 41 |
| Dickinson-a          | -0.665 81 | -0.410 15 |
| Scaled floating      | -0.666 10 | -0.410 92 |
| Dickinson-b          | -0.666 60 | -0.200 03 |
| Exact                | -0.667 53 | -0.667 53 |

In summary, the zero potential energy criterion  $E_{zp}$  introduced in this work is simply the Bartlett-Frost-Kellogg local energy<sup>3</sup> evaluated at those points in position space at which the potential energy operator vanishes, but it is a simple and convenient criterion to check the accuracy of wave functions, especially their long-range tails. In some cases, it may happen that different  $E_{zp}$ 's are found depending on different processes of  $\lim_{r \rightarrow 0}$ , but the occurrence of such situations itself can be said to be an indication of the inaccuracy of wave functions, when we invoke the spirit of the local energy formula.

## ACKNOWLEDGMENTS

I acknowledge the referee for his valuable comments. Part of this study has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

<sup>1</sup>B. H. Armstrong, Bull. Am. Phys. Soc. **9**, 401 (1964).

<sup>2</sup>A. J. Thakkar and V. H. Smith, Jr., Phys. Rev. A **18**, 841 (1978).

<sup>3</sup>J. H. Bartlett, Phys. Rev. **51**, 661 (1937); A. A. Frost, J. Chem. Phys. **10**, 240 (1942); A. A. Frost, R. E. Kellogg, and E. C. Curtis, Rev. Mod. Phys. **32**, 313 (1960).

<sup>4</sup>L. Pauling, Chem. Rev. **5**, 173 (1928).

<sup>5</sup>B. N. Finkelstein and G. E. Horowitz, Z. Phys. **48**, 118 (1928).

<sup>6</sup>A. C. Hurley, Proc. R. Soc. London Ser. A **226**, 170 (1954).

<sup>7</sup>H. Shull and D. D. Ebbing, J. Chem. Phys. **28**, 866 (1958).

<sup>8</sup>B. N. Dickinson, J. Chem. Phys. **1**, 317 (1933).

<sup>9</sup>R. L. Miller and P. G. Lykos, J. Chem. Phys. **37**, 993 (1962).

<sup>10</sup>F. Weinhold, J. Chem. Phys. **54**, 530 (1971).

<sup>11</sup>H. M. James, J. Chem. Phys. **3**, 9 (1935).

<sup>12</sup>J. Patel, J. Chem. Phys. **47**, 770 (1967).

<sup>13</sup>V. Guillemin, Jr. and C. Zener, Proc. Natl. Acad. Sci. U.S.A. **15**, 314 (1929).

<sup>14</sup>S. Kim, T. Y. Chang, and J. O. Hirschfelder, J. Chem. Phys. **43**, 1092 (1965).

<sup>15</sup>D. R. Bates, K. Ledsham, and A. L. Stewart, Philos. Trans. R. Soc. London Ser. A **246**, 215 (1953).

<sup>16</sup>R. Ahlrichs, M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and J. D. Morgan III, Phys. Rev. A **23**, 2106 (1981).

<sup>17</sup>W. Kutzelnigg and W. H. E. Schwarz, Phys. Rev. A **26**, 2361 (1982).