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Zero potential energy criterion for approximate wave functions

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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[1] and Thakkar and Smith[2] 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,[3] 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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

where $\lim_{V\to 0}$ 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 $V\to 0$ results from $\mathbf{r}\to\mathbf{0}$ (e.g., harmonic oscillator), Eq. (5b) takes a simple form,

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

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

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

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

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 $E_{\text{zm}}=E$ is a necessary but not sufficient condition for the "approximate" wave function to be the true wave function.[2] 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,[2] 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. Parameters 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 $1s$AO, 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 ζ 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.

		Parameters	
Wave function		$1s\sigma_g$ state	$2p\sigma_u$ state
Single hydrogenic 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 (Ref. 5)		$\zeta = 1.238\,70$	$\zeta = 0.900\,45$
Scaled floating (Refs. 6 and 7)		$\zeta = 1.242\,30$ $x = 0.093\,25$	$\zeta = 0.906\,55$ $x = -0.019\,06$
Dickinson (Refs. 8–10)			
	Case (a)	$\begin{cases}\zeta_1 = \zeta_2 = 1.254\,77 \\ c_2/c_1 = 0.160\,53\end{cases}$	$\zeta_1 = \zeta_2 = 0.905\,70$ $c_2/c_1 = -0.004\,83$
	Case (b)	$\begin{cases}\zeta_1 = 1.2459, \zeta_2 = 1.4826 \\ c_2/c_1 = 0.1379\end{cases}$	$\zeta_1 = 0.8356, \zeta_2 = 0.6325$ $c_2/c_1 = -0.0503$
James (Refs. 11 and 12)		$\delta = 1.353\,95$ $c = 0.447\,99$	$\delta = 0.900\,35$ $c' = 0.142\,69$
Guillemin–Zener (Refs. 13 and 14)		$a = 1.353\,9$ $b = 0.919\,1$	$a = 0.900\,3$ $b = 0.904\,2$
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	$E_{\rm av}$	$E_{\rm zm}$	$E_{\rm zp}$
Single 1*s*	− 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 $E_{\rm av}$ and $E_{\rm zp}$. Particularly, $E_{\rm zp}$ suggests the considerably wrong behavior of Dickinson-b function in its long-range region, so long as the parameters reported in the literature[10] 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 $E_{\rm av}$ and $E_{\rm zm}$ 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	$E_{\rm av}$	$E_{\rm zp}$
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 $E_{\rm zp}$ introduced in this work is simply the Bartlett–Frost–Kellog local energy[3] 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 $E_{\rm zp}$'s are found depending on different processes of $\lim_{V\to 0}$, 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.

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